

Access DB# 129042

SEARCH REQUEST FORM

Scientific and Technical Information Center

Requester's Full Name: Wayne Lange Examiner #: 60603 Date: 8-4-04
Art Unit: 1754 Phone Number: 302-21353 Serial Number: 101089689
Mail Box and Bldg/Room Location: E09A29 Results Format Preferred (circle): PAPER ~~DISK~~ ~~E-MAIL~~
Rensen

If more than one search is submitted, please prioritize searches in order of need.

Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc, if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of Invention: Method for preparing phosphorus pentoxide powder with enhanced fluidity

Inventors (please provide full names): Vincent Magae

Earliest Priority Filing Date: 8-2-00

For Sequence Searches Only Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.

*Please search claims 1-6,
as attached hereto.*

SCIENTIFIC REFERENCE BR
Sci & Tech Info. Cntr

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PTO-1590 (8-01)

S.N. 10/089689

10089689.091002

WO 02/12119

15

PCT/FR01/02527

CLAIMS

1. A process for the preparation of a phosphorus pentoxide (hexagonal variety) powder with improved flowability, characterized in that said
5 phosphorus pentoxide powder is subjected to mechanical stirring by the dry route at ambient temperature under a dry gas atmosphere for a period of time ranging from 5 minutes to 30 minutes.
2. The process as claimed in claim 1,
10 characterized in that the mechanical stirring time is between 10 and 20 minutes.
3. The process as claimed in either of
claims 1 and 2, characterized in that the stirring rate
of the device used for carrying out the process ranges
15 from 100 rev/min to 350 rev/min.
4. The process as claimed in claim 3,
characterized in that the stirring rate is between
150 rev/min and 300 rev/min.
5. The process as claimed in any one of
20 claims 1 to 4, characterized in that it is carried out at a temperature ranging from 15 to 30°C.
6. A phosphorus pentoxide (hexagonal
variety) powder obtained as claimed in one of claims 1 to
5, exhibiting a Hausner ratio Hr, defined as being the
25 ratio of the tamped apparent density d_t to the aerated
apparent density d_a , of equal to or less than 1.25.

=> file reg

FILE 'REGISTRY' ENTERED AT 15:19:01 ON 10 AUG 2004
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FILE 'REGISTRY' ENTERED AT 14:04:51 ON 10 AUG 2004
E PHOSPHORUS PENTOXIDE/CN
L1 1 SEA "PHOSPHORUS PENTOXIDE"/CN

FILE 'LCA' ENTERED AT 14:05:23 ON 10 AUG 2004
L2 32136 SEA (PRODUC? OR PROD# OR GENERAT? OR MANUF? OR MFR# OR
CREAT? OR FORM## OR FORMING# OR FORMAT? OR MAKE# OR
MADE# OR MAKING# OR FABRICAT? OR SYNTHESI? OR PREPAR? OR
PREP#)/BI,AB

FILE 'HCA' ENTERED AT 14:06:37 ON 10 AUG 2004
L3 4538 SEA L1/P OR L2(2A) (L1 OR (PHOSPHORUS# OR P) (W) (PENTOXIDE#
OR PENTAOXIDE#) OR P2O5)
L4 68358 SEA L1 OR (PHOSPHORUS# OR DIPHOSPHORUS# OR P) (W) (PENTOXID
E# OR PENTAOXIDE#) OR P2O5
L5 789749 SEA FLOW OR FLOWS OR FLOWED OR FLOWING# OR FLOWABIL? OR
FLOWABL?
L6 195134 SEA STIR OR STIRS OR STIRRED OR STRIRRING# OR STIRABIL?
OR STIRABL?
L7 16902 SEA (MECH# OR MECHANICAL?) (2A) (MIX? OR BLEND? OR AGITAT?
OR ADMIX? OR COMMIX? OR IMMIX? OR INTERMIX?)
L8 36687 SEA (REV# OR REVOLUTION?) (2A) (M OR MIN# OR MINUTE?) OR
RPM OR R(W)P(W)M
L9 82 SEA HAUSNER#
L10 1 SEA L4 AND L9
L11 1482 SEA L4 AND L5
L12 58 SEA L11 AND L6
L13 9 SEA L12 AND L3
L14 129 SEA L3 AND L6
L15 9 SEA L14 AND L5
L16 1 SEA L14 AND L7
L17 4 SEA L14 AND L8
L18 2929 SEA L4 AND L6
L19 58 SEA L18 AND L5
L20 9 SEA L18 AND L7
L21 44 SEA L18 AND L8
L22 129 SEA L18 AND L3

L23 75 SEA L4 AND L5 AND (L6 OR L7 OR L8)
L24 11 SEA L23 AND L3
L25 4 SEA L19 AND L21
L26 58 SEA L19 AND L23
L27 4 SEA L21 AND L23
L28 11224 SEA APPARENT?(3A) (D OR DENS?)
L29 390 SEA AERAT?(3A) (D OR DENS?)
L30 69 SEA L4 AND L28
L31 1 SEA L4 AND L29
L32 0 SEA L30 AND L31
L33 5 SEA L30 AND (L5 OR L6 OR L7 OR L8)
L34 31 SEA L10 OR L13 OR L15 OR L16 OR L17 OR L20 OR L25 OR L27
OR L31 OR L33
L35 1 SEA L24 NOT L34
L36 32 SEA L10 OR L13 OR L15 OR L16 OR L17 OR L20 OR L25 OR L27
OR L31 OR L33 OR L24
L37 37 SEA L21 NOT L36
L38 46 SEA (L12 OR L19 OR L26) NOT (L36 OR L37)
L39 15 SEA L23 NOT (L36 OR L37 OR L38)

=> file hca

FILE 'HCA' ENTERED AT 15:19:16 ON 10 AUG 2004

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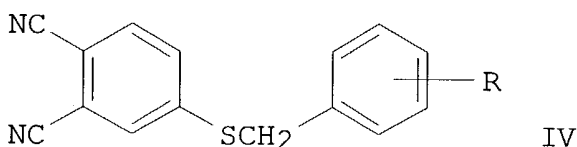
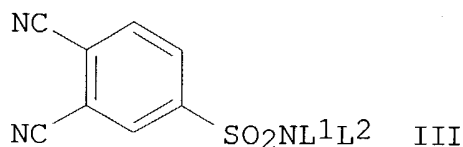
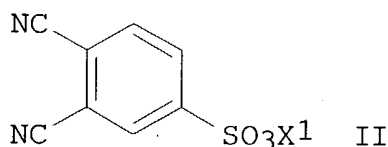
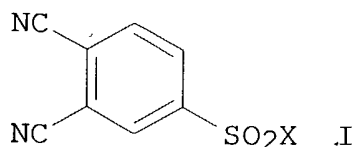
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=> d l36 1-32 cbib abs hitind

L36 ANSWER 1 OF 32 HCA COPYRIGHT 2004 ACS on STN

138:204840 Method for preparation of 4-halosulfonylphthalonitrile and
their conversion into 4-phthalonitrile derivatives. Terao, Koichi
(Seiko Epson Corp., Japan). Jpn. Kokai Tokkyo Koho JP 2003055335 A2
20030226, 16 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP
2001-248227 20010817.

GI



AB 4-Halosulfonylphthalonitrile (I; X = halo) undergoes hydrolysis in the presence of an acid or alkali to give 4-sulphophthalonitrile (3,4-dicyanobenzenesulfonic acid), reaction with alkali hydroxide to give 3,4-dicyanobenzenesulfonic acid salts [II; X1 = (Q)1/n; wherein Q = alkali or alk. earth metal, quaternary ammonium; n = a valency of Q], and amidation with amines to give 3,4-dicyanobenzenesulfonamides (III; L1, L2 = H, C1-4 alkyl). The starting material I is prepd. by contacting 4-benzylthiophthalonitrile derivs. (IV; R = H, C1-4 alkyl) with halogen mols. such as Br, Cl, and I in aq. acid soln. or org. solvent contg. H2O for halogenation. These processes readily give in high yields the 4-phthalonitrile derivs. which are useful as intermediates for phthalocyanine compds. widely used for printer inks and optical recording materials. Thus, 25.0 g 4-benzylthiophthalonitrile was dissolved in a soln. of 210 mL AcOH and 40 mL H2O and cooled to 5-10°, followed by introducing 22.5 g Cl into the soln. at 5-10° over 1 h, and the resulting mixt. was **stirred** at the same temp. for 1 h, poured into ice-water, and **stirred** for .apprx.1 h to give, after filtering the pptd. crystals, successively washing them with H2O and isopropanol, and drying at 40° under the **flow** of air to give 16.6 g 4-chlorosulfonylphthalonitrile (V). V (4.1 g) was added portionwise to 40 mL 28% aq. NH3 at 5-10° under ice-cooling, **stirred** at room temp. overnight (8 h), adjusted to pH 1-2 adding dropwise concd. HCl to give, after filtering the pptd. crystals, washing them with distd. water, and drying at 50° under the **flow** of air to give 2.6 g 4-sulfonamidophthalonitrile (3,4-dicyanobenzenesulfonamide).

IC ICM C07C303-02

ICS C07C303-22; C07C303-38; C07C309-57; C07C311-16; C07B061-00

CC 25-20 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)
Section cross-reference(s): 26

IT 75-44-5, Phosgene 603-35-0, Triphenylphosphine, reactions

1314-56-3, Phosphorus pentoxide,
reactions 10025-87-3, Phosphorus oxychloride
(**prepn.** of bromophthalonitrile by dehydration of
bromophthalamide with dehydrating agent)

L36 ANSWER 2 OF 32 HCA COPYRIGHT 2004 ACS on STN

136:169897 **Preparation of phosphorus**

pentoxide powder with enhanced fluidity by mechanical
treatment. Magne, Vincent (ATOFINA, Fr.). PCT Int. Appl. WO
2002012119 A1 20020214, 18 pp. DESIGNATED STATES: W: AE, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM,
EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG,
KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TT, TZ, UA,
UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM; RW:
AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB,
GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR.
(French). CODEN: PIXXD2. APPLICATION: WO 2001-FR2527 20010802.
PRIORITY: FR 2000-10348 20000804.

AB **Phosphorus pentoxide** powder **produced**
by air oxidn. of white phosphorus is treated mech. to enhance its
fluidity. The **P2O5** powder is **mech.**

agitated under a dry gas atm. at 15-30°C for 10-20
min at a rotation velocity of 150-300 **rpm.** The obtained
hexagonal **P2O5** powder has a **Hausner** ratio of
≤ 1.25.

IC ICM C01B025-12

CC 49-2 (Industrial Inorganic Chemicals)

ST **phosphorus pentoxide** powder **mech**

agitation fluidity enhancement

IT **Flow**

(enhancement of; **prepn.** of **phosphorus**
pentoxide powder with enhanced fluidity by mech.
treatment)

IT **Powders**

(**flow** enhancement of **P2O5**; **prepn.**
of **phosphorus pentoxide** powder with enhanced
fluidity by mech. treatment)

IT **Air**

(oxidant; **prepn.** of **phosphorus**
pentoxide powder with enhanced fluidity by mech.
treatment)

IT **Agitation (mechanical)**

(**prepn.** of **phosphorus pentoxide**
powder with enhanced fluidity by mech. treatment)

IT **1314-56-3P, Phosphorus pentoxide,**

preparation

(mech. treatment of; **prepn.** of **phosphorus**

- pentoxide** powder with enhanced fluidity by mech. treatment)
- IT 7723-14-0, Phosphorus, reactions
(white, oxidn. of; **prepn.** of **phosphorus pentoxide** powder with enhanced fluidity by mech. treatment)
- L36 ANSWER 3 OF 32 HCA COPYRIGHT 2004 ACS on STN
- 132:333918 Manufacture of calcium superphosphate from defluorinated slag. Wu, Zhaoqiang; Zeng, Deren; Ai, Xincheng; Peng, Zhigao; Xu, Changshou (Phosphorous Calcium Fertilizer Plant, Weiyuan County, Peop. Rep. China). Faming Zhuanli Shenqing Gongkai Shuomingshu CN 1206701 A 19990203, 7 pp. (Chinese). CODEN: CNXXEV. APPLICATION: CN 1998-111987 19980427.
- AB The raw material of the calcium superphosphate is composed of ground phosphorite (contain 34% of **P2O5**) 30-35%, defluorinated slag (contain 22-28% of **P2O5**) 30-35%, H₂SO₄ 25%, and water 10-15%. The content of **P2O5** in the **produced** calcium superphosphate is 16-20%. The process comprises mixing, and allowing all ingredients to react at 105-125° for 20-30 min to obtain fresh calcium superphosphate, and curing to obtain fluffy product. The **flow** rates of H₂SO₄ and ore slurry, the temp. of the ore slurry, and the free acid (**P2O5**) content in the ore slurry are controlled to 1, 3.5 m³·h⁻¹, 110-135°, and 15-18% resp. while mixing. The fresh calcium should be **stirred** every 8 h at 60-80° during May-August and every 24 h at 50-80° in other months resp. while curing.
- IC ICM C05B011-08
- CC 19-6 (Fertilizers, Soils, and Plant Nutrition)
- L36 ANSWER 4 OF 32 HCA COPYRIGHT 2004 ACS on STN
- 128:16100 Isothermal oxidation of white phosphorus dispersed in water in a **stirred**-tank reactor. Mathews, Joseph B.; Jefcoat, Irvin A. (Olin Chem. Corp., Charleston, TN, USA). Journal of the Air & Waste Management Association, 47(10), 1103-1110 (English) 1997. CODEN: JAWAFC. Publisher: Air & Waste Management Association.
- AB A global, first-order kinetic model fit data for the isothermal wet oxidn. of elemental white P (P₄) in a batch, **stirred**-tank reactor. The initial white phosphorus solids concn. was held const. at 1 g/L while an air **flow** of 2.0 std. L/min supplied O for the reaction. A CD6-like turbine and an A2 impeller were evaluated at speeds from 1000-2250 **rpm**. For the CD6-like turbine, mass transfer effects were assumed to be eliminated above 2000 **rpm**; thus, the CD6-like turbine with a speed of 2250 **rpm** was selected for isothermal studies. Particle size and temp. were varied. For isothermal conditions, the first order

kinetic const. was 0.022/min at 46° to 0.078/min at 80°. The apparent activation energy was 6.78 kcal/mol. O reacted with suspended P₄ particles forming oxides of P, primarily **phosphorus pentoxide** (P₄O₁₀ or P₂O₅).

Some of the **P₂O₅** reacted with water to form PO₄³⁻ as the primary product of white P oxidn. The amt. of **phosphorus pentoxide** absorbed in water increased with temp. The rate of PO₄³⁻ formation followed zero order kinetics and was independent of particle size. As temp. increased, the PO₄:PO₃ ratio increased. This observation and the apparently low activation energy suggested that diffusion effects may not have been completely eliminated.

CC 60-2 (Waste Treatment and Disposal)

Section cross-reference(s): 49, 67

ST isothermal oxidn white phosphorus; **stirred** tank reactor

oxidn white phosphorus; kinetics isothermal oxidn white phosphorus

IT Wastewater treatment

(oxidn., isothermal wet; particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred**-tank reactor)

IT Oxidation kinetics

(particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred**-tank reactor)

IT Phosphates, processes

(particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred**-tank reactor)

IT Solid wastes

(white phosphorus contg.; particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred**-tank reactor)

IT **1314-56-3, Phosphorus pentoxide,**
processes

(particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred**-tank reactor)

IT 12185-10-3, White phosphorus, processes

(particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred**-tank reactor)

IT 7782-44-7, Oxygen, reactions

(particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred**-tank reactor)

L36 ANSWER 5 OF 32 HCA COPYRIGHT 2004 ACS on STN

120:326859 Removal of heavy metals especially cadmium, lead and mercury from extractive phosphoric acid. Teren, Jan; Hutar, Eduard; Gabco,

Milan (Czech Rep.). Czech. CS 275029 B2 19920115, 9 pp. (Czech).
CODEN: CZXXA9. APPLICATION: CS 1989-1494 19890310.

AB Heavy metals are removed from crude H_3PO_4 by pptn. in the form of sulfides at 15-95°. The reaction mixt. is **stirred** by circulation, pneumatic **mixing**, and/or **mech. mixing**, substances accelerating clarification are optionally added, and the pptd. sludge is sepd. by settling, filtration, centrifuging, and/or flotation. Before, during, and/or after adding a source of the sulfidic S, $4.2 + 10^{-4} - 4.6 + 10^{-1}$ mol NH_3 , KOH, and/or NaOH/mol H_3PO_4 is added. NH_3 is added in the form of $NH_3(g)$, $NH_3(l)$, or NH_4OH . The procedure is esp. suitable for H_3PO_4 used for fertilizer manuf. Thus, crude H_3PO_4 was treated with 5 g 13% Na_2S soln./kg H_3PO_4 and 25 g 25% NH_4OH /kg H_3PO_4 . The Cd content decreased from 79.9 to 2.3 mg/kg **P205**, and Pb content decreased from 0.56 mg/kg **P205** to trace.

IC ICM C01B025-237

CC 49-2 (Industrial Inorganic Chemicals)
Section cross-reference(s): 19

L36 ANSWER 6 OF 32 HCA COPYRIGHT 2004 ACS on STN

115:236161 Phosphorosulfide-containing compounds and their use as lubricant additives. Andress, Harry John, Jr.; Ashjian, Henry (Mobil Oil Corp., USA). Eur. Pat. Appl. EP 445970 A2 19910911, 5 pp. DESIGNATED STATES: R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE. (English). CODEN: EPXXDW. APPLICATION: EP 1991-301665 19910228. PRIORITY: US 1990-488581 19900305.

AB Lubricating compns. comprise a major proportion of a lubricating oil or grease and a minor amt. of the reaction products of C2-32-olefins with free S, with or without added H_2S , P_2S_5 , and **P205**, **prepd.** by reacting the olefins and the S in the molar ratio 1:2 to 2:1 with approx. 0.1-1 mol P_2S_5 and P_2O_5 , and, optionally, an aliph. amine and/or alkene oxide. The compns. are manufd. by reacting S, with or without added H_2S , with a C2-32-olefin, P_2S_5 , and P_2O_5 , at 50-150° under autogenous pressure in the above mol. ratios. These compns. have improved antiwear properties. A mixt. of S 11, P_2S_5 0.5, isobutylene 10, and H_2S 5 mols was heated in an autoclave at 120° for 12 h, and cooled to 25°, after which 1.2 mol propylene oxide was added. The reaction mixt. was **stirred** at 50° for 8 h, after which 0.4 mol Primene 81R was added and the mixt. **stirred** at 50° for 2 h. In a (described) test at 390°F, base lubricating oils contg. 1 wt.% of the additives gave scar diam. at 500, 1000, 1500, and 2000 **rpm** 0.4, 0.4, 0.5, and 0.6, vs. 1.0, 1.31, and 2.08 mm, and not available, resp., for base oil not contg. the additive.

IC ICM C10M159-12

CC 51-8 (Fossil Fuels, Derivatives, and Related Products)

IT 115-11-7D, Isobutylene, reaction products with hydrogen sulfide and

phosphorus pentoxide and pentasulfide and sulfur 1314-56-3D, **Phosphorus pentoxide, reaction products** with hydrogen sulfide and olefins and phosphorus pentasulfide and sulfur mixts. 1314-80-3D, Phosphorus pentasulfide, reaction products with hydrogen sulfide and olefins and phosphorus pentoxide and sulfur mixts. 7704-34-9D, Sulfur, reaction products with hydrogen sulfide and olefins and phosphorus pentoxide and pentasulfide and sulfur mixts. 7783-06-4D, Hydrogen sulfide, reaction products with olefins and phosphorus pentoxide and pentasulfide and sulfur mixts.

(lubricating oil additives contg., for decreased wear)

L36 ANSWER 7 OF 32 HCA COPYRIGHT 2004 ACS on STN

94:183357 Color proof films. Liu, Shuchen (American Hoechst Corp., USA). Eur. Pat. Appl. EP 19896 19801210, 26 pp. (German). CODEN: EPXXDW. APPLICATION: EP 1980-102931 19800527.

AB As material for color proofs of the type of (CA 63: 15770a), esp. with dark shades, of high sensitivity, good support-coating adhesion, and scratch-resistivity, 40-80 μ polyester supports are coated with a 0.1-10 μ o-quinone-sensitized dyed or pigmented layer which contains 10-60% of an anionic H₃PO₄ mono- or diester surfactant (CA 56: 3585i), having a d. of 1.0-1.4 (25°), a **flow point** of <30°, and an acidity of 55-120 mg KOH per g to reach pH 5.0-5.5. The surfactants are reaction **products** of P2O₅ with a condensate of a C₆-150 compd., such as a phenol, contg. ≥ 1 mol of a C₂-4 alkylene oxide. The foils are UV-exposed through a pos. screened Ag color sepn. image, developed with an alk. soln., and then given an overall exposure to remove the yellow tint due to residual sensitizer. In neg.-working coatings the surfactants shorten the developing time. Thus, a Me methacrylate-methacrylic acid 85:15 copolymer 5.1 g was dissolved in MeOCH₂CH₂OH, **stirred** for 1 h with Orasol Yellow 3 GLG 0.86, Orasol Black 6.02, 2,3,4-trihydroxybenzophenone naphthoquinone-(1,2)-diazide-(2)-5-sulfonate 12.04, and GAF Gafac RE-610 surfactant 6.00 g, then filtered for coating a 76 μ biaxially oriented polyester support. Exposure through a pos. color sepn. and a step wedge for 20 s and development with aq. 9% Na lauryl sulfate, followed by a 20 s after-exposure, resulted in a pos. black sepn. image revealing 2 steps. Without the surfactant an exposure of 320 s was required to produce the same result.

IC G03F003-10; G03F007-08

CC 74-2 (Radiation Chemistry, Photochemistry, and Photographic Processes)

L36 ANSWER 8 OF 32 HCA COPYRIGHT 2004 ACS on STN

87:72431 Suspension for manufacturing foundry molds. Ivanov, V. N.; Chulkova, A. D. (Moscow Automobile Plant, USSR). Belg. BE 840650 19761012, 25 pp. (French). CODEN: BEXXAL. APPLICATION: BE

1976-166073 19760412.

AB Foundry molds with good mold-release properties, strength, dimensional stability, and life were prep'd. from suspensions contg. an alkyl silicate binder 2.5-9, water 16.5-23, HCl 0.05-0.25, phosphoric acid deriv. 0.2-1.0, surfactant with plasticizing action 0.02-0.1%, and the balance refractory filler (av. particle size $<50\mu$). Thus, a suspension of HCl (d. 1.15 g/cm³) 355, Cr Al phosphate (**P2O5**/(Al₂O₃ + Cr₂O₃) ratio 2.3) 415 cm³, Et silicate 40 (d. 1.05 g/cm³) 3.2 L, disodium sulfosuccinate [14933-03-0] 100 g, and powd. quartz 44 kg in 14.9 L water was **stirred** at 2800 rpm for 60 min. The viscosity of a 100 cm³ sample of the suspension **flowing** through a 4 min diam. orifice was 45 s which increased to 50 s after 48 h storage. A layer of the suspension was dried for 3 h and had flexure strength 57 and 107 kg/cm² at 20 and 900°, resp. After 48 h storage at 17°, the values were 52 and 103.5 kg/cm², resp.

IC B22C

CC 57-5 (Ceramics)

Section cross-reference(s): 55

L36 ANSWER 9 OF 32 HCA COPYRIGHT 2004 ACS on STN

87:25464 Trisodium monophosphate dodecahydrate with cubelike or beadlike crystal form. Liedloff, Bernd; Gisbier, Doris (Ger. Dem. Rep.). Ger. (East) DD 121502 19760805, 7 pp. (German). CODEN: GEXXA8. APPLICATION: DD 1975-188206 19750905.

AB Aq. H₃PO₄ is reacted at 70-80° with aq. NaOH to give a soln. having Na/P atom ratio of 3.1-3.3, sp. gr. 1.31-1.34, and **P2O5** 11-13%. The soln. is then **stirred** (Froude no. 0.026-0.062) and cooled during 16-23 to 30-40°. The product is free-**flowing**. It effloresces more slowly in air at 25-45° and also cakes less during storage than Na₃PO₄.12H₂O needle crystals. Thus, 3.9 m³ of H₃PO₄ having sp. gr. 1.61 and 8.8 m³ of aq. NaOH having sp. gr. 1.50 were added simultaneously to 25 m³ of spent liquor (5% **P2O5**) contained in a crystallizer of 38 m³ capacity. The reaction temp. was 70-80° and the final reaction soln. had Na/P ratio of 3.18, sp. gr. 1.328 and contained 12.5% **P2O5**. It was cooled to 35.5° over 20 h while stirring at 30 rpm with a 1.6-m-diam. stirrer (Froude no. 0.04) to give a solids yield of 85.5% of the Na₃PO₄.12H₂O which was in soln. The **product** contained **P2O5** 18.6, Cl 0.01, and insols. 0.02%. The sieve anal. was 1 mm, 2.1; 0.2-0.5 mm, 91.2; and <0.2 mm 6.7%.

IC C01B025-18

CC 49-5 (Industrial Inorganic Chemicals)

L36 ANSWER 10 OF 32 HCA COPYRIGHT 2004 ACS on STN

86:70779 Density, viscosity, and surface tension of nitroammophos and nitroammophoska melts. Nikandrova, Ya. T.; Artyushina, A. I.;

Avdyakova, O. S.; Nikandrov, I. S. (USSR). Tezisy Dokl. Vses. Nauchno-Tekh. Konf. Tekhnol. Neorg. Veshchestv Miner. Udobr., 9th, Volume 1, 58. Editor(s): Amirova, S. A. Permsk. Politekh. Inst.: Perm, USSR. (Russian) 1974. CODEN: 34PSAU.

- AB The H₂O content (0-5.5%) had no effect on the d. of the melt at 140-185°. When KCl was added the **apparent** d. decreased (at 180°) by a factor of 1.1 and when KNO₃ or K phosphate (10% K₂O) was added the **apparent** d. increased by 30-40 kg/m³. Equations describing the temp. relations of the nitroammophos and nitroammophoska melt d. and viscosity are presented. The energy of activation of the viscous flow decreased with H₂O content increasing (0.5-5.5%). When the H₂O content increased to 10% the activation energy increased to 8.5 kcal/mole; the melt viscosity increased 1.2-1.3-fold when even 2.4% K₂O was added. A linear relation between surface tension of the melts and temp. and a decrease in the surface tension with increasing K₂O content of the melt were obsd. At 170° and H₂O content 2%, the d. of nitroammophos having a N/P₂O₅ ratio 1:1 was 1508 kg/m³; its viscosity and surface tension were 0.0107 nsec/m² and 0.1037 nsec/m, resp.
- CC 19-5 (Fertilizers, Soils, and Plant Nutrition)
Section cross-reference(s): 49

L36 ANSWER 11 OF 32 HCA COPYRIGHT 2004 ACS on STN

76:49612 Treating digestion tank water to remove phosphorus compounds. Dunseth, Maria G.; Brinkman, Joel J. (W. R. Grace and Co.). Ger. Offen. DE 2123669 19711125, 16 pp. (German). CODEN: GWXXBX. PRIORITY: US 19700513.

- AB At least 80% by wt. total P is removed from digestion tank water when kept 30-120 min at 60-75° at atm. pressure or at at least 55°/710 mm or at lesser temp. and pressure and the solid matter is sepd. from the water. In treatment of water in which the proportion of hard ions is stoichiometrically less than that required theoretically for pptn. of the contained phosphates as orthophosphate salts, the addn. of MgO is suggested. Thus, a 2-1. sample of sewage contg. 120, 100, 80, 70, and 330 mg/l. Ca, Mg, total P, orthophosphate, and total N heated at 65° and **stirred** 2 hr at 100 rpm with increase of pH from 7.0 to 8.8, centrifuged and analyzed showed elimination of 95% total P and 77% total N. The BOD and COD diminished from 297 to 130 mg/l. and from 560 to 364 mg/l., resp. The residual solids contained 19.5% P₂O₅ in a **form** suitable for use by plants.

IC C02C

CC 60 (Sewage and Wastes)

Section cross-reference(s): 61

L36 ANSWER 12 OF 32 HCA COPYRIGHT 2004 ACS on STN

74:41489 Continuous preparation of an aqueous ammoniated phosphate

composition. Mullen, George C., Jr. (Standard Oil Co.). U.S. US 3459499 19690805, 8 pp. (English). CODEN: USXXAM. APPLICATION: US 1966-546411 19660429.

AB In production of ammonium polyphosphate soln. by reacting NH_3 and wet-process superphosphoric acid (which contains polyphosphates), it is important to avoid hydrolysis of the polyphosphate because otherwise the metal compds. sequestered by the polyphosphate will ppt. In the process claimed, the NH_3 and superphosphoric acid are introduced at points remote from each other into a large body of **stirred** ammonium polyphosphate soln. In an example, NH_3 and H_2O in the required amts. were introduced into a stream of recycled soln. and the mixt. **flowed** into the reactor where wet-process superphosphoric acid (72% **P2O5**) was sparged in. Good quality product soln. (10% N, 33.5% **P2O5**) was **produced**; <1% of the polyphosphate was hydrolyzed.

IC C01B; C05B

NCL 023107000

CC 20 (Fertilizers, Soils, and Plant Nutrition)

L36 ANSWER 13 OF 32 HCA COPYRIGHT 2004 ACS on STN

73:47141 Low density ammonium polyphosphates. (Knapsack A.-G.). Fr. Demande FR 2009787 19700206, 6 pp. (French). CODEN: FRXXBL. PRIORITY: DE 19680531.

AB Long chain NH_4^+ polyphosphates having the general formula $(\text{NH}_4)_n + 2\text{PnO}_3\text{n} + 1$ are prep'd. by treating polyphosphoric acid with NH_3 at $310-30^\circ$. Thus, 5.035 kg polyphosphoric acid (84% **P2O5**) at 90° is treated with 1.5 std. m^3 NH_3/hr , and the mixt. is held at $310-20^\circ$. After 30 min, when neutralization is complete, NH_3 **flow** is reduced to 0.4 m^3/hr , and the mixt. is held at 245° to sep. a melt in less than an hr. The mixt. is cooled, washed with H_2O (to ext. short chain polyphosphates), and dried under vacuum at 70° to recover 5.28 kg of cryst. product (I) contg. 72.8% **P2O5** and having an **apparent d.** 0.39 kg/l. with $n = 110$. Also, $n = 350$ when 50 kg I (at 30 kg/hr) is heated for 50 min at 310° in an NH_3 atm.

IC C01B

CC 49 (Industrial Inorganic Chemicals)

L36 ANSWER 14 OF 32 HCA COPYRIGHT 2004 ACS on STN

71:128426 Purification of recirculating waters of the "Fosforit" Kingisepp plant concentrating mill. Shifrin, S. M.; Varyukha, D. N. (USSR). Sanit. Tekh., 7-12. Editor(s): Shifrin, S. M. Leningrad. Ordena Trudovogo Krasnogo Znameni Inzh.-Stroit. Inst.: Leningrad, USSR. (Russian) 1967. CODEN: 21IRAS.

AB Water which has been used in the process of beneficiation of phosphate ore, contained up to 85,000 mg./l. of suspended solids and materials used in flotation both org. and inorg. Purification was

carried out by (a) sedimentation, (b) coagulation with polyacrylamide 0.1 mg./l. as coagulant, (c) biocoagulation by using activated sludge 0.1 ml./l. and **aeration** for 70 min., (d) biol. purification with the activated sludge process. Sedimentation decreased the amt. of suspended solids to 477.2 mg./l. in 30 min. and to 229.3 mg./l. in 60 min. Further increase in the time of sedimentation did not give any significant improvement. Coagulation (b) gave an effluent contg. 60 mg./l. of suspended solids after 30 min. of sedimentation. Biocoagulation removed 65% of suspended solids. In biol. purification, NH_4Cl 20 mg./l. and Na phosphate 10 mg./l. of **P205** were added and treatment was carried out on a lab. scale in cylindrical tanks of 56-l. capacity. The whole was aerated from 12 to 25 hrs. The treatment lowered B.O.D. from .apprx.300 to 11 mg./l.

CC 60 (Sewage and Wastes)

L36 ANSWER 15 OF 32 HCA COPYRIGHT 2004 ACS on STN

71:12458 Synthesis and selection of catalysts for the oxidation of propylene to acrolein. Lemberanskii, R. A.; Aliev, V. S.; Kyazimov, Sh. K.; Efendiev, R. M. (USSR). Azarbaycan Neft Tasarrufati, 48(1), 34-6 (Russian) 1969. CODEN: AZNKAY. ISSN: 0365-8554.

AB The oxidn. of C_3H_6 to acrolein was studied in a lab. flow-through glass reactor under the following conditions: duration of the expts. 30-1500 hrs., temp. 425-500°, contact time 1.74-2.35 sec., and the content of C_3H_6 in the gas-air mixt. 1.87-25.0 vol. %. The catalysts investigated contained Bi_2O_3 (10.29-62.8 wt. %), MoO_3 (3.21-37.2 wt. %), and **P205** (0.0-0.5 wt. %) supported on silica gel, $\alpha\text{-Al}_2\text{O}_3$, and corundum. Following compds. were found in the reaction products: acrolein 45.0-84.0, HCHO 0.227-6.66, MeCHO 0.45-13.22, MeCO_2H 0.56-12.5, CO_2 3.70-32.4, CO 0.0-7.6, and H_2O 3.4-10.2 wt. %. The conversion was 10.7-52.0 wt. % based on C_3H_6 . Best results (conversion 34-5 wt. %, selectivity for acrolein 72-4 wt. %) were obtained at 500°, contact time 2 sec., and 25.0 vol. % C_3H_6 in the gas-air mixt. on the catalyst contg. Bi_2O_3 11.5, MoO_3 8.02, and **P205** 0.5 wt. % supported on corundum (bulk d. 2.055 g./cm.³, **apparent d.** 3.09 g./cm.³, porosity 21%, and the sp. surface area 0.6-1.2 m.²/g.).

CC 23 (Aliphatic Compounds)

IT 1304-76-3 1313-27-5, uses and miscellaneous **1314-56-3**
(catalysts, for oxidn. of propene)

L36 ANSWER 16 OF 32 HCA COPYRIGHT 2004 ACS on STN

66:117466 Productive use of phosphate slurry. (Knapsack A.-G.). Neth. Appl. NL 6608852 19670116, 10 pp. (Dutch). CODEN: NAXXAN. PRIORITY: DE 19650714.

AB The slurry obtained by neutralization of wet process H_3PO_4 with alkali to pH 4-10 can be used economically when mixed with finely

ground phosphate ore and made into shaped pieces for electrolytic production of P, provided the mixt. contains <15% slurry by wt. on dry basis. The slurry consists of phosphates of Fe, Al, Ca, and Mg, with .apprx.60% of H2O both occluded and as H2O of crystn. The dry material contains .apprx.50% **P2O5**. The slurry is **stirred** with H2O, or with the usual binders or fillers, e.g. clay, phosphate powder, or finely divided phosphate and alkali phosphates, so as to give a mixt. contg. 25-40% solids by wt., and this is then mixed with the phosphate ore, which is pressed into shapes or granulated, dried at 300-400°, and sintered. In this way the **P2O5** in the slurry, may be obtained as P, the pressure- and abrasion-resistance of the granules or other solid forms are increased, and the use of binders may be avoided or decreased. In an example, 10 kg. phosphate slurry assocd. with 60% H2O by wt., was suspended in 60 kg. H2O in a mixing vessel to give a comparatively easy **flowing** mixt. contg. 25% dry material; 350 kg. of ground phosphate ore was granulated with 100 kg. of this mixt. in a rotary granulator. The moist granules contained 16.5% H2O by wt. and .apprx.8.9% dried slurry on the basis of the phosphate ore. After drying and sintering at .apprx.950° the granules had a pressure resistance at the center of 75-80 kg. and an abrasion resistance of 85-90% detd. by rolling 1000 kg. of sintered pellets for 30 min. in a 300 mm. diam. cylinder at 80 **rpm**. and finding the amt. with size <0.5 mm.

IC C01B

CC 49 (Industrial Inorganic Chemicals)

L36 ANSWER 17 OF 32 HCA COPYRIGHT 2004 ACS on STN

66:96941 Concentration of aqueous solutions and suspensions. (SINCAT Societa Industriale Catanese S.p.A.). Neth. Appl. NL 6608226 19661219, 18pp. (Dutch). CODEN: NAXXAN. PRIORITY: IT 19650618.

AB The soln. or suspension to be concd. is dispersed in a rapid stream of hot gases rising in a container with increasing cross section. The rate of **flow** of the gas thus gradually diminishes until conditions become favorable for the formation of a fluidized bed of drops with practically stable dimensions, in which the drops come into very efficient direct contact with the gas, and are rapidly concd. at a comparatively low temp. As they lose H2O, the drops become smaller and their **apparent d.** sometimes decreases, and they are then carried along by the gas. They are cooled and may easily be sepd. at the outlet, e.g., by a cyclone separator. In the app. described, gases at 70-1100° pass into the lower section of a practically vertical elongated vessel having a constriction above the gas inlet, in which the gases reach a velocity of 50-70 m./sec., followed by a section with an upward increase in diam. having the form of a truncated cone with included angle 6-9°. A section with const. diam. follows, joined by a tube with decreasing diam., in which the gases are again

accelerated, to a bend leading to the separator. The soln. or suspension is introduced at the constriction. The occurrence of incrustations on the walls and of blockages is largely avoided. Thermal equil. is rapidly established, and the gas remains in contact with the liquid during the concg. stage for only some tenths of a sec. Good results are obtained with solns. of H_3PO_4 , H_2SO_4 , hydroxides, Na_2CO_3 , NaHCO_3 , $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, KNO_3 , KCl , K_2SO_4 , $\text{Ca}(\text{NO}_3)_2$, MgSO_4 , MgCl_2 , and fertilizer suspensions from which a granulated product may be manufd. From substances with a low m.p. a molten product may be obtained at the outlet. In H_3PO_4 concn. the formation of mist is avoided, and starting with 30% **P205** by wt. a product with 64% **P205** may be obtained. Operating conditions can be changed rapidly, and when it suddenly becomes necessary to store the product, production of highly concd. acid gives best use of available storage facilities. In concg. 30% H_3PO_4 contg. 2% F to 50% **P205** by wt., 70-5% of the F is removed, and 90% when concg. to 64%. The F compds. are comparatively easy to recover from the residual gases. Because of rapid concn., app. with small dimensions can give high production. The gases used in the process can be air heated in a combustion chamber, or various waste gases from other processes which would be normally discharged to the atm., provided they have a low moisture content, a suitable temp., and do not react with the substances to be concd. In an example, a concentrator was used consisting of a vertical Venturi tube with a 500 mm. long narrow portion with internal diam. 214 mm. The included angle of the diffusor was 7° . Above the Venturi tube was a tube with a const. diam. of 500 mm. The product was sepd. in a cyclone and collected at its exit. Approx. 2210 standard m.³ of air/hr. at 650° was used with a velocity of .apprx.49 m./sec. in the constriction, and .apprx.5 m./sec. at the exit from the diffusor. A soln. (1365 kg./hr.) at 65° contg. 43% $(\text{NH}_4)_2\text{SO}_4$ and 57% H_2O was fed in at the constriction and .apprx.965 kg./hr. of a suspension contg. 25.4% crystd. $(\text{NH}_4)_2\text{SO}_4$, 35.9% $(\text{NH}_4)_2\text{SO}_4$ soln., and 38.7% H_2O was obtained.

IC B01D

CC 48 (Unit Operations and Processes)

L36 ANSWER 18 OF 32 HCA COPYRIGHT 2004 ACS on STN

66:30583 Preparation of phosphoric acid. (Societe PROREA). Neth. Appl. NL 6600968 19660803, 24 pp. (Dutch). CODEN: NAXXAN. PRIORITY: FR 19650203 - 19650903 19650903.

AB Improved filtration during wet process manuf. of H_3PO_4 is obtained by dispersing broad, flat, very thin streams of H_2SO_4 into a well-**stirred** circulating phosphate slurry. Addn. of natural phosphate can immediately precede or follow addn. of H_2SO_4 , depending on its reactivity and fineness. Conditions can be regulated so that H_3PO_4 and $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ are formed, with $x = 2, 1/2$, or 0. Preferably $x = 2$, and the formation of gypsum crystals is

avored by the immediate and practically complete dispersion of the H_2SO_4 , which avoids pptn. of anhydrite and α -semihydrate, and the formation of too many seed crystals of gypsum, allowing the crystals already present to grow more regulary. If the temp. of the slurry is brought to .apprx. 70° immediately after dispersion of the H_2SO_4 , crystals with dimensions 200-300 μ are formed. When this temp. is brought initially above 70° , a microscopic ppt., probably of unstable β -semihydrate, is formed, and if the temp. is then suddenly reduced to 70° at the outflow from the dispersion vessel, this avoids formation of α -semihydrate, which would take 10-36 hrs. to be transformed to gypsum, and the gypsum crystals already present then grow at the expense of the ppt. to attain dimensions 800-1000 μ . The cooling can be achieved by rapid mixing of the circulating slurry with wash water from the sepn. of the H_3PO_4 and gypsum, or with slurry cooled to 70° by blowing in air or by vacuum evapn. When, simultaneously with the addn. of natural phosphate, H_2SO_4 and wash water are dispersed close together in the same vessel, the temp. may be controlled so that gypsum crystals form with dimensions .apprx. 600 μ . Finally an amt. of slurry is withdrawn from circulation corresponding to the production of H_3PO_4 and gypsum, and these are sepd., e.g. by filtration or centrifugation. A plant for the process is described consisting of a series of vessels through which the circulating slurry **flows**, and in the 1st of which the initial reactions take place, to be concluded in the following vessels in which ripening of the slurry takes place, part of which is withdrawn for sepn. of H_3PO_4 and the crystals formed. Connecting lines are provided between the ripening and reaction vessels, and with a circuit through a vacuum evaporator, to enable electronic control of the regulating valves to bring the temp. to the desired value. The vessel in which the initial reactions take place consists of divisions, in the 1st of which phosphate is added to the slurry, and in the 2nd of which the H_2SO_4 is dispersed. A single vessel may be used for the addn. of phosphate and the simultaneous dispersion of H_2SO_4 and wash water. A special dispersion app. is described having openings or small channels next to one another so as to disperse H_2SO_4 and wash water mixed completely at the moment at which they come into contact with the slurry. This dispersal unit also **stirs** the medium, and has a hollow axle and blades with sep. channels for H_2SO_4 and wash water, which come together at the ends of the blades and are simultaneously dispersed. Scoops, the height of which is adjustable, may be fitted above the dispersal zone for thorough stirring. In the plant described 9.5 kg./hr. of Moroccan phosphate with 34% **P2O5** and 8.9 kg./hr. 98% H_2SO_4 were added. The primary slurry circulated at 190 kg./hr. The temp. at the outlet from the H_2SO_4 disperser was 88° , and the crystn. temp. in the 2nd and 3rd vessels was $70-2^\circ$, and $69-70^\circ$ in the 4th. H_3PO_4 was **produced** with 32% **P2O5**

and 2.5% H₂SO₄. Easily filterable diamond-shaped crystals with dimensions 800-1000 μ were formed. The total yield of P₂O₅ was 98.5%.

IC C01B

CC 49 (Industrial Inorganic Chemicals)

L36 ANSWER 19 OF 32 HCA COPYRIGHT 2004 ACS on STN

64:57922 Original Reference No. 64:10795d-g Wet-process phosphoric acid and utilization of the by-product gypsum. Roy, A. K.; Bardhan, M. K.; Singh, R. U. (Fertilizer Corp. India, Ltd., Sindri). Technology (Sindri, India), 2(2), 71-5- (English) 1965. CODEN: TCNOAQ. ISSN: 0040-1641.

AB The prepn. of phosphoric acid from Makatea and Morocco varieties of rock phosphate was studied. The suitability of the by-product gypsum obtained was compared with 2 com. samples of by-product gypsum for the production of (NH₄)₂SO₄. In the usual process, rock phosphate is treated with H₂SO₄ in the presence of recycle phosphoric acid; gypsum is a by-product. Since the quantity of gypsum is about 4.5 tons per ton of P₂O₅ produced, its disposal is a major problem in the industry. The Merseburg process involves the reaction of gypsum with (NH₄)₂CO₃ to make (NH₄)₂SO₄. In the absence of indigenous sources of S in India, the production of (NH₄)₂SO₄ from by-product gypsum is attractive because the sulfate radical is used twice. Thus, 75 g. rock phosphate (80% through 100 mesh B.S.) was placed in a 3-neck stirred 3-l. flask, maintained at 70 \pm 5°. Phosphoric soln. of measured concn. and vol. was then added and the mixt. was stirred for 4-5 min. at 90 rpm. Dil. H₂SO₄ was then added slowly with a slight increase in the stirrer speed. During the reaction, a slight vacuum, 12 mm. of H₂O, was maintained on the reaction flask. After the reaction, the slurry was filtered under a vacuum of 20 in. Hg through a No. 1 Whatman filter paper and the filtration time noted. Filter cakes were washed with dil. phosphoric acid and finally with distd. H₂O. The washed cakes were dried at 45° and analyzed. A reaction time of 4 hrs. was found to give the best filterability and min. residual F and P₂O₅ in the gypsum. The conversion efficiency with Morocco phosphate was slightly better than with the Makatea variety. Gypsum from the former also had better filterability. The filterability of the magma is the most important factor in detg. the suitability of a particular gypsum for reaction with (NH₄)₂CO₃ soln. By this criteria, the 2 by-product gypsum samples from the Morocco and Makatea varieties of rock phosphate appear to be better suited for conversion to (NH₄)₂SO₄ than the 2 com. samples, but not as well suited as a sample of natural gypsum from Pakistan.

CC 17 (Industrial Inorganic Chemicals)

L36 ANSWER 20 OF 32 HCA COPYRIGHT 2004 ACS on STN

64:27167 Original Reference No. 64:4963h,4964a-h,4965a-g
Polyfluorobicyclo[2.2.1]heptanes. I. 1H-Undecafluoro- and
1H,4H-decafluorobicyclo[2.2.1]heptane and a novel elimination
process. Campbell, S. F.; Stephens, R.; Tatlow, J. C. (Univ.
Birmingham, UK). Tetrahedron, 21(11), 2997-3008 (English) 1965.
CODEN: TETRAB. ISSN: 0040-4020.

GI For diagram(s), see printed CA Issue.

AB cf. CA 62, 16076f. Bicyclo[2.2.1]heptadiene (200 g.) passed over 6
kg. CoF₃ at 250-300° in 3 hrs. and the product removed in a
stream of N at 30 l./hr. in 1.5 hrs., trapped at -78° and the
H₂O-washed **product** dried over **P2O5**, the
product (2.3 kg. from 5 runs) distd. through a
vacuum-jacketed column packed with Dixon gauze rings and the
fractionation controlled by gas chromatography over 1:2 dinonyl
phthalate-kieselguhr (unit A) (100°, N **flow-rate**
1.0 l./hr.) gave fractions 1, b. 27-66° (130 g., 6
components); 2, b. 66-73° (172.3 g., 2 components); 3, b.
73-4.9° (210 g., 2 components); 4, b. 74.9-5.1° (99
g.); 5, b. 75.1-83.0° (162 g., 5 components); 6,
83-6.8° (116 g., 3 components); 7, b. 86.8-91° (161.6
g., 4 components); 8, b. 91-5° (206 g., 3 components); 9, b.
95-109.5° (146.8 g., 5 components); 10, b. 109.5-12°
(148.9 g., 2 components); 11, b. 112° (284.3 g.); and 217 g.
unidentified residue. Fraction 2 (8 g.) sepd. on unit A
(70°, N **flow-rate** 14 l./hr.) gave 4 g.
perfluoromethylcyclohexane and 2.5 g. perfluorobicyclo[2.2.1]heptane
(I), m. 105-7° (sealed tube). Similar sepn. of fraction 3 (6
g.) gave 4.5 g. impure perfluoromethylcyclohexane and 0.7 g. I.
Sepn. of 160 g. fraction 7 on a 1:2 dinonyl phthalate-kieselguhr Cu
column (488 + 7.5 cm., unit C) at 92° with 40 l./hr. N
flow-rate gave 60 g. 1H-undecafluorobicyclo[2.2.1]heptane
(II), m. 94-6° (sealed tube). Fraction 8 (200 g.) taken up
in C₆H₆ and sepd. on unit C at 82°, N-**flow-rate** 44
l./hr. yielded 130 g. II. Similar sepn. of fraction 10 (140 g.) in
Et₂O yielded 95 g. 1H,4H-decafluorobicyclo[2.2.1]heptane (III), m.
92-3° (sealed tube), b. 112°. Fraction 11 distd. from
P2O5 gave 280 g. III with correct ir spectrum. The
substantial yield reflected the high chem. stability associated with
a bridgehead hydrogen. II (2 g.) slowly sublimed in a stream of N
(3.5 l./hr.) passing over **stirred** CoF₃ at 250°, the
product collected at -180° and sepd. on unit A at 90°
in N at 17 l./hr. gave 0.6 g. I and 0.2 g. II. Similar fluorination
of 2.0 g. III gave 0.3 g. I and 0.4 g. II. Similar fluorination of
2.0 g. III gave 0.3 g. I and 0.4 g. II. Both II and III were
recovered unchanged after treatment with strong aq. KOH at
100° but underwent extensive deuteration when treated with
KOH in D₂O. II (2 g.), 10 g. KOH, and 10 g. D₂O shaken 3 hrs. at
100° in a sealed Pyrex glass tube and the lower layer distd.

in vacuo gave 1.8 g. 80% deuterated material m/e 276, 275, 176, 175, 226, 225, reconverted to II on shaking 3 hrs. at 100° with KOH and H₂O. Similar deuteration of 3 g. III gave 2.7 g. 70% deuterated material, m/e 259, 258, 257, 209, 208, 207, 178, 177, 176, 159, 158, 157, indicating the presence of .apprx.57% 1D,4D-decafluorobicyclo[2.2.1]heptane, 38% 1H,4D-decafluorobicyclo[2.2.1]heptane, and 5% III. The exchanges showed the transient formation of the carbanion (IV) under the purely inductive influence of 3 > CF₂ groups in a satd. system without resonance stabilization of the anion by neighboring unsatd. groups. The general validity of the method of deuteration was indicated by comparable exchanges with C₆H₅F (70%), 1H-nonafluorocyclohexene (65%), and F₃CCHBrCl (95%). II (6 g.) in 80 ml. Et₂O **stirred** at -40° with dropwise addn. of 0.98N MeLi in Et₂O and evolution of 420 ml. CH₄, the mixt. **stirred** at -40° 30 min. and treated with 20 ml. redistd. AcH, the mixt. **stirred** 30 min. at -40° and 1 hr. at 20°, dild. with 25 ml. 4N HCl and the washed and dried Et₂O evapd., the residue (10.5 g.) analyzed over 1:2 silicone-gum-kieselguhr (unit B) and sepd. on a Cu column contg. 1:2 silicone-gum-kieselguhr gave 3.0 g. undecafluorobicyclo[2.2.1]heptylmethylcarbinol (V), m. 99-100°. V (0.5 g.) and a trace of hydroquinol distd. from P205 gave 0.3 g. undecafluorobicyclo[2.2.1]heptylethylene, m. 49-50°. Other successful trapping expts. demonstrated the existence of the anion IV. With D₂O at -55° the mixt. from treatment of II with MeLi in Et₂O at -40° yielded 60% 1-deuterioundecafluorobicyclo[2.2.1]heptane, characterized by ir and N.M.R. spectroscopy. Br and MeBr at -55° similarly yielded 68% 1-bromoundecafluorobicyclo[2.2.1]heptane, m. 109-10°, and 1-methylundecafluorobicyclo[2.2.1]heptane, m. 125.5-6.5°. It was of considerable interest to exam. the thermal stability of IV. II (6 g.) in 400 ml. Et₂O at -55° **stirred** with dropwise addn. of 1.1N MeLi (prepd. from MeI) in Et₂O and the mixt. **stirred** 30 min. at -55°, kept 30 min. at 25-30° and refluxed gently 1 hr., filtered from pptd. LiF and the residue on evapn. sepd. by gas chromatography on a 1:2 silicone-gum-kieselguhr column gave a mixt. (2.4 g.) of Et₂O and 2 minor components, sepd. on unit A to give small amts. of the olefin, 1H-nonafluorobicyclo[2.2.1]hept-2-ene (VI), and 4.8 g. 1-iodononafluorobicyclo[2.2.1]hept-2-ene (VII), b. 124-5°. VI (0.5 g.) and KMnO₄ in Me₂CO gave HO₂CCF₂CF₂CO₂H, isolated as its dianilinium salt (0.25 g.), m. 210-11°. VII (1 g.) passed over CoF₃ at 280° in a stream of N and the product (0.9 g.) washed with H₂O and distd. in vacuo over P205 gave 0.5 g. I, showing retention of the norbornane skeleton. VI (0.9 g.) fluorinated over CoF₃ at 140° gave 0.6 g. II. VII (3 g.) in 15 ml. Et₂O **stirred** with 10 g. Mg in 90 ml. Et₂O contg. a small crystal of iodine and the mixt. refluxed 2 hrs., treated

slowly with 30 ml. 3N H₂SO₄ and the isolated product (5.2 g.) sepd. on unit A gave 1.4 g. VI, m. 36-7°. An estn. of the stability of an ethereal soln. of the Li salt of IV was made by dividing the soln. at -55° into 3 parts of which the 1st was treated with AcH at -40° to give a 40% yield of V. The 2nd portion was kept 30 min. at 15° and then treated with AcH, giving 10% V and 18% VII. The 3rd portion was refluxed 1 hr. before addn. of AcH and gave 40% yield of VII only. The decompn. at 15° is much slower than that associated with non-bridgehead carbanions. II (1 g.) treated with MeLi (from MeBr) in 30 ml. Et₂O at -55° and the system **stirred** 1 hr. at 20° with addn. of 10 g. D₂O, the filtered dried Et₂O layer evapd. in vacuo and the residue (3.3 g.) sepd. by gas chromatography on unit A gave 0.6 g. 1D-undecafluorobicyclo[2.2.1]heptane, ir spectrum differing in the range 3000-650 cm.⁻¹ from that of II. The decompn. of Li salt of IV to VII presumably involves initial loss of F ion in a non-coplanar β -elimination to give a transient bridgehead olefin (VIII) or diradical of very short duration. Addn. of LiI (known to be present in ethereal MeLi prepd. from MeI) and loss of F ion from the adduct in a very facile cis-coplanar elimination gives VII. II (6 g.) in 400 ml. Et₂O at -55° **stirred** with addn. of 1.03N MeLi (from MeBr) in Et₂O and the isolated residue (6.3 g.) sepd. (3.5 g.) on a preparative scale gave 0.5 g. 9:1 mixt. of 1-methyl-undecafluorobicyclo[2.2.1]heptane (IX) and suspected 1-methyl-nonafluorobicyclo[2.2.1]hept-2-ene, together with 1.3 g. 1-bromononafluorobicyclo[2.2.1]hept-2-ene (X), b. 100°, contg. a small amt. of 1-bromoundecafluorobicyclo[2.2.1]heptane (XI). X (1 g.) in 5 ml. Et₂O added dropwise with stirring to 0.3 g. Mg in 30 ml. gently refluxing Et₂O and the mixt. refluxed 1.75 hrs., **stirred** with 25 ml. 4N H₂SO₄ and the washed, dried, and filtered Et₂O layer evapd. in vacuo gave 1.9 g. residue sepd. by gas chromatography over unit A column at 65° to give 0.5 g. VI. Fluorination of X over CoF₃ at 200° gave 90% yield of XI, whereas fluorination of VII resulted in complete substitution of the iodine. II (2 g.) in 50 ml. Et₂O at -55° treated dropwise with stirring with N MeLi (from MeBr) and the soln. **stirred** 30 min. at -55°, **stirred** with addn. of 6 g. Br and the mixt. **stirred** 30 min. at -55° and at 20° 1 hr., dild. with 10 ml. H₂O and treated with Na₂S₂O₃, the washed and dried filtered Et₂O soln. evapd. and the residue (3.4 g.) sepd. by chromatography on unit B yielded 1.7 g. XI, m. 109-10°. II (1 g.) in 50 ml. Et₂O at -55° **stirred** with dropwise addn. of 0.93N MeLi (from MeBr) and the mixt. **stirred** 30 min. at -55°, bubbled through 30 min. with MeBr at -55° and at 25-30° 30 min., the soln. refluxed gently 30 min. and the cooled, washed and dried soln. freed from Et₂O and excess MeBr, the residue (1.7 g.) sepd. on column B from 1.0 g. Et₂O and gave 0.5 g. IX, m. 125.5-6.5°.

together with a trace of X. The same starting mixt. without passage of MeBr gave 1.8 g. residue, sepd. chromatographically to yield (from 1 g. II), 0.1 g. IX and 0.5 g. X. Further evidence for the operation of the proposed mechanism was provided by decompn. of the Li salt of IV in the presence of furan. II (3 g.) in 50 ml. Et₂O at -55° **stirred** with dropwise addn. of 0.93N MeLi (from MeBr) and **stirred** 30 min. at -55°, **stirred** with dropwise addn. of 10 ml. redistd. furan and the mixt. **stirred** 30 min. at -55° and kept 30 min. at 25-30°, the system **stirred** 1 hr. under gentle reflux and the filtered soln. freed from Et₂O, sepd. by vapor phase chromatography and the 1.6 g. waxy adduct (XII) analyzed by chromatography on unit B column showed the presence of 2 roughly equal components, m. 70-90°, m/e 343, 66, τ 6.5 s, 5.3 s, 6.4 m, 5.1 m, ν 1300-1200 cm.⁻¹ (KBr). The formation of 2 closely similar structures would be expected from Diels-Alder addn. of furan to a bridgehead olefin.

CC 34 (Alicyclic Compounds)

L36 ANSWER 21 OF 32 HCA COPYRIGHT 2004 ACS on STN

61:87798 Original Reference No. 61:15304a-c Nitric phosphate fertilizers. (Asahi Chemical Industry Co., Ltd.). GB 970946 19640923, 8 pp. (Unavailable). PRIORITY: JP 19601005.

AB In the process for the manuf. of fertilizers by digesting phosphate rock with a mixt. of HNO₃ and H₂SO₄ or K₂SO₄, ammoniating the reaction mixt., and drying, an improvement comprises conducting the digestion in 2 stages, thereby permitting regulation of the Ca:SO₄²⁻ ratio so that the byproduct gypsum is produced in readily filterable form and the viscosity remains low. For example, 60% HNO₃ 1933, and K₂SO₄ 716 kg./hr, were continuously mixed, and the mixt. was fed to a 1st digestion stage concurrently with 450 kg./hr, phosphate rock. The Ca in the rock was equiv. to the SO₄²⁻ in the acid mixt. The temp. was 45° and the retention time was 30 min. The slurry **flowed** to a 2nd digestion stage where an addnl. 468 kg./hr. phosphate rock was added. The temp. was 50° and the retention time was 45 min. The slurry from the 2nd stage contained gypsum crystals 50-300 μ long, and the viscosity was 0.5-1.5 poises. Ammoniation was then carried out to pH 3.2, and the slurry was concd. to 10% H₂O; the viscosity at this stage was 35 poises (100°, 20 r.p.m.). Granulation and drying yielded a **product** contg. total P₂O₅ 10.69, H₂O-sol. P₂O₅ 3.01, N 13.9, K₂O 12.1, CaO 15.99, SO₃ 10.47, and H₂O 1.5%. As an alternate procedure the gypsum can be filtered out before ammoniation. Brit. 970,947; 7 pp. In the process of the preceding abstr. a portion of the slurry or filtrate from the 2nd digestion is recirculated to the 1st digestion, thereby aiding the growth of gypsum crystals.

IC C01B

CC 73 (Fertilizers, Soils, and Plant Nutrition)

L36 ANSWER 22 OF 32 HCA COPYRIGHT 2004 ACS on STN

60:68186 Original Reference No. 60:11995e-h,11996e-f Oxygen isosteres of carcinogenic hydrocarbons. I. Synthesis of benzobis(benzofurans). Dingankar, P. R.; Gore, T. S. (Univ. Bombay). Indian Journal of Chemistry, 2(2), 71-3 (Unavailable) 1964. CODEN: IJOCAP. ISSN: 0019-5103.

GI For diagram(s), see printed CA Issue.

AB The title compds. were synthesized for study of their carcinogenic activity. A soln. of 10 g. 2,5-dichlorohydroquinone in 100 ml. abs. MeOH was added to a soln. of 2.6 g. Na in 50 ml. abs. MeOH, the mixt. refluxed 15 min., and the alc. removed in vacuo to give 2,5-dichlorohydroquinone Na salt (I). 2-Bromocyclohexanone (II) (21 g.) and 200 ml. dry C₆H₆ were added to I and the mixt. shaken mech. 72 hrs. under N. Addn. of 30 ml. 2% aq. NaOH gave 13 g. 1,4-bis(2-oxocyclohexyloxy)-3,6-dichlorobenzene (III), m. 236° (2,4-dinitrophenylhydrazine m. 242°). A mixt. of 10 g. P₂O₅ and 20 ml. phosphoric acid (d. 1.7) was heated 1 hr. at 200° and cooled, 1 g. III added, and the mixt. stirred 3 hrs. at 100° and poured into 100 g. crushed ice to give 0.7 g. 6,12-dichloro-1,2,3,4,7,8,9,10-octahydrobenzo[1,2-b:4,5-b']bis(benzofuran) (IV), m. 241-2°. IV (0.16 g.) and 0.12 g. Pd-C (10%) was heated 1.5 hrs. at 200° and then 4 hrs. at 280-300°. The product sublimed in the condenser was benzo[1,2-b:4,5-b']bis(benzofuran) (IVa) (0.1 g.), m. 267-8°. Similarly, condensation of the di-Na salt of 2,3-dichlorohydroquinone (from 5 g. of the dichlorohydroquinone) with 10.5 g. II by shaking 72 hrs. in dry C₆H₆ gave 6 g. 1,4-bis(2-oxocyclohexyloxy)-2,3-dichlorobenzene, m. 250° (BuOH), which on cyclodehydration (as for IV) gave 6,7-dichloro-1,2,3,4,9,10,11,12-octahydrobenzo[1,2-b:4,3-b']bis(benzofuran) (V), m. 299-300° (BuOH). V (0.2 g.) on heating 5 hrs. with 0.15 g. Pd-C (10%) at 320-40° under N gave benzo[1,2-b:4,3-b']bis(benzofuran) (Va), m. 139° (BuOH). Similar condensation of the di-Na salt of 4-chlororesorcinol (from 7.5 g. 4-chlororesorcinol) with 18 g. II gave 7 g. of the dioxo compd., which failed to crystallize, but which, in Me₂CO and CHCl₃ refrigerated several days, gave 1,3-bis(2-oxocyclohexyloxy)-4-chlorobenzene, m. 157°, which on cyclodehydration (as for IV) gave 2 g. 6-chloro-1,2,3,4,8,9,10,11-octahydrobenzo[1,2-b:3,4b']bis(benzofuran) (VI), m. 154° (BuOH). Finally, dehydrogenation of 0.5 g. VI with 0.25 g. Pd-C (10%) (as in IV) gave 0.3 g. benzo[1,2-b:3,4-b']bis(benzofuran) (VIa) m. 164-5° (BuOH). Similarly, 6,12-dimethylbenzo [1,2-b:4,5-b']bis(benzofuran) (VII), m. 254° (obtained by C₆H₆ extn.), and 6,12-dimethylbenzo[1,2b:5,4-b']bis(benzofuran) (VIII), m. 174° (BuOH) were synthesized from 2,5-dimethylhydroquinone

and 2,5-dimethylresorcinol, resp. In these 2 cases, however, the oxo compds. were unstable and could not be isolated. The products of condensation were the cyclized compds. 6,12-dimethyl-1,2,3,4,7,8,9,10-octahydrobenzo[1,2-b:4,5-b']bis(benzofuran), m. 262° (BuOH) and 6,12-dimethyl-1,2,3,4,8,9,10,11-octahydrobenzo [1,2-b:5,4-b']bis(benzofuran), m. 192° (BuOH), resp., which on dehydrogenation gave VII and VIII in excellent yields.

CC 38 (Heterocyclic Compounds (More Than One Hetero Atom))

L36 ANSWER 23 OF 32 HCA COPYRIGHT 2004 ACS on STN

59:44696 Original Reference No. 59:8090b-d Nitrogen-containing superphosphate. Ch'en, Wei-Ts'ang Huaxue Tongbao (No. 8), 38-42 (Unavailable) 1960. CODEN: HHTPAU. ISSN: 0441-3776.

AB Hair is washed with water and slowly immersed in 60%, H₂SO₄ (1 kg./kg, hair), heated at 90°, and **stirred** for 10 min. to a black liquid consisting of a mixt. of various amino acids and excess H₂SO₄. Fresh bones are ground to a particle size of about 5 mm., placed in a kettle with water and are heated under 1.5-2 atm. pressure in the kettle; the resultant glue is from time to time replaced by water. Then the bones are dried and milled. The bone meal is mixed with the black liquid obtained, and the mixt. is heated at 70° in a Beskov chamber for 20 min. After cooling, the superphosphate formed is cut out in the usual manner. The product, contg, amino acids, Ca(H₂PO₄)₂.H₂O, CaSO₄, and CaSO₄.1/2H₂O, is a dark gray powder having a pleasant odor and is stable on prolonged storage. Chem. compn. of the **product** (in %) assimilable **P2O5** ≥ 18, N ≥ 8; moisture ≤ 15, free acidity ≤ 5.5. The dil. soln. of glue obtained as a by-product can be hydrolyzed with H₂SO₄ like the hair, or evapd. to get a glue, in which case the supernatant fatty layer of liquid must be first removed. The method of analysis is described.

CC 73 (Fertilizers, Soils, and Plant Nutrition)

IT Water, analysis
(detn. in free-flowing powders)

IT Powders
(free-flowing, water detn. in)

L36 ANSWER 24 OF 32 HCA COPYRIGHT 2004 ACS on STN

57:42519 Original Reference No. 57:8429i,8430a-i,8431a-i,8432a-e Dinitroacetonitrile. II. Derivatives of dinitroacetonitrile from Michael, Mannich, and alkylation reactions. 2,2-Dinitro-2-cyanoethanol and its derivatives. Parker, Charles O.; Emmons, William D.; Pagano, Angelo S.; Rolewicz, Henry A.; McCallum, Keith S. (Rohm & Haas Co., Huntsville, AL). Tetrahedron, 17, 89-104 (Unavailable) 1962. CODEN: TETRAB. ISSN: 0040-4020.

AB Addn. of HC(NO₂)₂CN (I) to carbonyl conjugated unsatd. systems was a

generally successful reaction for the prepn. of Michael adducts. I tetrahydrate (II, 24.0 g.) and 17.2 g. $\text{H}_2\text{C}:\text{CHCO}_2\text{Me}$ heated 5 hrs. at 50° in 35 ml. MeOH, kept 16 hrs. at 20° , the volatile material evapd. in vacuo, the residue taken up in Et_2O , the washed and dried soln. evapd., and the residual liquid (8.4 g.) flash distd, at $100-20^\circ/0.05$ mm. yielded 21% distillate, redistd. to give a sample of $(\text{O}_2\text{N})_2\text{C}(\text{CN})\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ (III), b0.12-0.15 $78-80^\circ$, n_D 1.4595. III (1.2 g.) refluxed 3 hrs. in 15 ml. 20% HCl and the solid product (91%) recrystd. from H_2O (C) yielded $(\text{CH}_2\text{CO}_2\text{H})_2$ m. $186-9^\circ$. $\text{NaC}(\text{NO}_2)_2\text{CN}$ (12.5 g.) in 250 ml. Et_2O **stirred** 30 min. with dropwise addn. of 4.2 g. H_2SO_4 at 20° , the filtered soln. treated with 5.8 g. recrystd. $\text{H}_2\text{C}:\text{CHCONH}_2$ together with some EtOAc, the soln. refluxed 24 hrs., the filtered soln. evapd., the partially cryst. residue (12 g.) taken up in alc., and the filtered soln. dild. with C_6H_6 gave 5.9 g. material, m. $43-5^\circ$ recrystd. 3 times from CHCl_3 -alc. to give 29% $(\text{O}_2\text{N})_2\text{C}(\text{CN})\text{CH}_2\text{CH}_2\text{CONH}_2$, m. $62-3^\circ$. II (28.5 g.) and 14.5 g. $\text{H}_2\text{C}:\text{CHCO}_2\text{H}$ (IV) kept 48 hrs. at $25-35^\circ$ in 15 ml. H_2O , the volatile material evapd. in vacuo, the solid (29.6 g., m. $95-112^\circ$) recrystd. from 1:1 CHCl_3 - C_6H_6 , and the cryst. material (60%, m. $104-9^\circ$) recrystd. 4 times from Et_2O - CHCl_3 (C) gave $(\text{O}_2\text{N})_2\text{C}(\text{CONH}_2)\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ (V), m. $115-17^\circ$. The filtrate from the CHCl_3 - C_6H_6 crystn. evapd. and the product fractionated yielded 13% $(\text{O}_2\text{N})_2\text{C}(\text{CN})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, m. $73-4^\circ$ (CHCl_3). IV (40 g.) and 8.0 g. II kept 14 hrs. in 11 ml. Me_3COH , the solvent evapd. in vacuo, the residue triturated with CHCl_3 , and filtered yielded 69% slightly impure V, m. $111-13^\circ$. $\text{NaC}(\text{NO}_2)_2\text{CN}$ (10.0 g.) in 80 ml. EtOAc **stirred** 30 min. with dropwise addn. of 3.3 g. H_2SO_4 at 20° , the filtered soln. kept 12 hrs. at 40° with 5.0 g. IV, the solvents removed in vacuo, and the residue (15 g.) extd. with Et_2O and CHCl_3 yielded 34% α,α -dinitroglutarimide (VI), recrystd. from H_2O and twice from EtOAc- C_6H_{12} to give a sample, m. $146-8^\circ$, v 3160, 3060, 1578 cm^{-1} . V (0.7 g.) in 30 ml. MeCN **stirred** 2 hrs. with excess P205 (exothermic reaction), the solvent evapd., the residue extd. with Et_2O , and the product (46%, m. $148-50^\circ$ recrystd. from EtOAc- CHCl_3 gave VI, m. $150-1^\circ$. II (9.2 g.) kept 40 hrs. in 10 ml. H_2O contg. 2.8 g. $\text{H}_2\text{C}:\text{CHCHO}$, the oily layer (96%) taken up in 30 ml. MeOH, refluxed 5 hrs. with 9.4 g. $\text{HC}(\text{OMe})_3$ and 0.08 g. p- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$, and the volatile material evapd. in vacuo gave 66% yellow liquid, distd. to yield 57% $(\text{O}_2\text{N})_2\text{C}(\text{CN})\text{CH}_2\text{CH}_2\text{CH}(\text{OMe})_2$, b0.4 $80-1^\circ$. The adduct from another run flash distd. yielded 31% impure $(\text{O}_2\text{N})_2\text{C}(\text{CN})\text{CH}_2\text{CH}_2\text{CHO}$, b0.75-1.30 $80-92^\circ$. The diversity of products from IV was accounted for most readily by postulating cyclization of the normal adduct. II (0.044 mole) **stirred** 15 hrs. at $35-40^\circ$ in 250 ml. MeOH with 0.016 mole recrystd. 1,3,5-triacryloylperhydro-s-triazine, the solvent evapd., the residue taken up in alc., and

dild. with CHCl_3 yielded 26% 1,3,5-tris(γ,γ -dinitro- γ -cyanobutyl)perhydro-s-triazine, m. 143° . II (0.123 mole) **stirred** 7 hrs. at 55° with 0.065 mole recrystd. methylenebisacrylamide in 300 ml. H_2O , most of the solvent evapd. in vacuo, the residue taken up in a min. of alc., and dild. with H_2O yielded 31% $[(\text{O}_2\text{N})_2\text{C}(\text{CN})\text{CH}_2\text{CH}_2\text{CONH}]_2\text{CH}_2$, m. $134-5^\circ$ (aq. alc.). MeCOCH:CH_2 (5.0 g.) and 12.0 g. II in 15 ml. H_2O kept 5 days at 20° , the oily layer (92.5%) washed 3 times with 35 ml. H_2O , taken up in Et_2O , the dried (MgSO_4) soln. evapd., the residue flash distd. at $100-4^\circ/0.5-1.0$ mm. to give 68% distillate, n_{20D} 1.4650, and redistd. through a falling film still at $77^\circ/0.2-0.5$ mm. gave 5,5-dinitro-5-cyano-2-pentanone, n_{20D} 1.4646, v 2245, 1721, 1599, 1297 cm^{-1} ; semicarbazone m. $137-8^\circ$ (decompn.) (aq. alc.). Under rather limited environmental conditions, N-(2,2-dinitro-2-cyanoethyl)amides were prepd. through the reaction of I with N-methylolamides. In all expts. I was used as obtained by neutralizing $\text{NaC}(\text{NO}_2)_2\text{CN}$ in EtOAc with an equiv. of H_2SO_4 , stirring the mixt. 30 min., and using the filtered soln. BzNHCH_2OH (5.0 g.) in 30 ml. EtOAc **stirred** 2 hrs. at 50° with dropwise addn. of 0.033 mole I in 50 ml. EtOAc , the mixt. kept 30 min. at 50° the cooled mixt. freed from volatile material in vacuo, the residue extd. with CH_2Cl_2 , the filtered ext. evapd., and the residue (20%, m. $117-18^\circ$) recrystd. from CCl_4 and twice from C_6H_6 gave $\text{BzNHCH}_2\text{C}(\text{NO}_2)_2\text{CN}$, m. $119.5-20.5^\circ$. AcNHCH_2OH (8.1 g.) in 30 ml. EtOAc **stirred** with 0.09 mole I in EtOAc and 5 g. anhyd. MgSO_4 , the soln. warmed to 30° kept 2 hrs., the filtered soln. evapd. in vacuo, the residue shaken with 2-3 vols. ice H_2O , decanted, the residue taken up in Et_2O , the dried soln. evapd., and the product (5.5 g., m. $70-3^\circ$) recrystd. from C_6H_6 gave $\text{AcNHCH}_2\text{C}(\text{NO}_2)_2\text{CN}$, m. $76.5-7.5^\circ$. MeCH:CHCONH_2 (4.25 g.) and 1.5 g. paraformaldehyde ground together with addn. of 2 drops of nearly satd. aq. K_2CO_3 , grinding continued 2-3 min., the mixt. heated to $50-60^\circ$ with stirring, the cooled mixt. taken up in 40 ml. dioxane, the filtered soln. **stirred** with addn. of 14 g. powd. Drierite, **stirred** 2 hrs. at $40-5^\circ$ with dropwise addn. of 0.05 mole I in 50 ml. EtOAc , the mixt. kept 30 min. at $40-5^\circ$, the cooled filtered soln. freed from volatile material in vacuo, the viscous residue triturated in ice H_2O , and the dried solid (3.3 g., m. $70-3^\circ$) recrystd. from C_6H_6 yielded 27% $\text{MeCH:CHCONHCH}_2\text{C}(\text{NO}_2)_2\text{CN}$, m. $74-5^\circ$. Similarly, 0.05 mole $\text{H}_2\text{C:CHCONH}_2$ gave 20% $\text{H}_2\text{C:CHCONHCH}_2\text{C}(\text{NO}_2)_2\text{CN}$, m. $77-8^\circ$ (C_6H_6). $(\text{HOCH}_2\text{NH})_2\text{CO}$ (0.11 mole) and 0.075 mole anhyd. MgSO_4 **stirred** 5 hrs. at 12° with dropwise addn. of 0.22 mole I in EtOAc , the residue on evapn. of the filtered soln. triturated with cold H_2O , the dried product extd. with Et_2O , the product (1.5 g., m. 127°) extd. with boiling ClCH:CHCl and boiling $\text{Cl}_2\text{CHCH}_2\text{Cl}$, the residue taken up in Et_2O , and the soln.

dild. with petr. ether gave $\text{OC}[\text{NHCH}_2\text{C}(\text{NO}_2)_2\text{CN}]_2$, m. 136° .
Formalin (250 ml., 37%) treated portionwise with 76.5 g.
 $\text{NaC}(\text{NO}_2)_2\text{CN}$, **stirred** 30 min. with dropwise addn. of 27.8
ml. chilled concd. H_2SO_4 at $23-6^\circ$ (ice bath), the mixt. kept
4 days at 20° , and extd. 4 times with 50 ml. Et_2O yielded 95%
 $\text{HOCH}_2\text{C}(\text{NO}_2)_2\text{CN}$ (VII), n₂₀D 1.4470. $(\text{CF}_3\text{CO})_2\text{O}$ (0.113 mole) and 1.0
g. $\beta\text{-C}_{10}\text{H}_7\text{OH}$ treated dropwise at 30° (ice bath) with
0.113 mole anhyd. **MeCH**: CHCO_2H , the **mixt.**
stirred 5 min., **stirred** at $20-30^\circ$ with
dropwise addn. of 0.087 mole VII, the **mixt.** **stirred** 1 hr.,
poured into 500 ml. ice H_2O , extd. with 200 ml. Et_2O , the **mixt.**
neutralized with solid Na_2CO_3 , the aq. layer extd. twice with 50 ml.
 Et_2O , the combined washed and dried Et_2O soln. evapd., and the ester
(79%) flash distd. yielded 32% **MeCH**: $\text{CHCO}_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{CN}$, b_{0.07}
 $53-8^\circ$, v 2260, 1740, 1602 cm^{-1} Similarly, 0.13 mole
 $(\text{CF}_3\text{CO})_2\text{O}$, 0.13 mole AcOH , and 0.10 mole VII yielded 57% acetate,
distd. in vacuo to give 34% product, b_{1.0} $71-92^\circ$,
fractionated to yield 26% pure $\text{AcOCH}_2\text{C}(\text{O}_2\text{N})_2\text{CN}$, b_{1.25} $73-5^\circ$,
n₂₀D 1.4439, d₂₀ 1.335. CHCl_3 (50 ml.), 3.5 g. VII, 1.3 g. AlCl_3 ,
and 1.0 g. $(p\text{-HOC}_6\text{H}_4)_2\text{NH}$ **stirred** at $24-7^\circ$ (cooling)
with addn. of 1.8 g. $\text{H}_2\text{C}:\text{CHCOCl}$, the **mixt.** heated 1 hr. at
 $30-5^\circ$ and 1 hr. at $35-40^\circ$ with rapid evolution of HCl ,
the cooled **mixt.** poured into 500 ml. ice H_2O , the aq. layer extd.
with 300 ml. CHCl_3 , the filtered CHCl_3 washed with 1% aq. NaHCO_3 ,
and the dried soln. evapd, in vacuo gave 3.2 g. product, distd. to
yield 49% $\text{H}_2\text{C}:\text{CHCO}_2\text{CH}_2\text{C}(\text{O}_2\text{N})_2\text{CN}$, b_{0.1} $56-60^\circ$, v 1750, 1600
 cm^{-1} Concd. HNO_3 (42 g.) and 63 g. concd. H_2SO_4 treated dropwise
at $0-5^\circ$ (ice salt bath) with 300 ml. and twice with 50 ml.
 Et_2O , the Et_2O washed with 50 ml. 1% aq. NaHCO_3 and 3 times with 50
ml. H_2O , and the dried soln. evapd. yielded 67% product. Distn. of
a sample in vacuo gave the nitrate ester, b_{0.1} $46-55^\circ$, v
1600, 1678 cm^{-1} , becoming acidic fairly rapidly on standing.
 $(\text{CF}_3\text{CO})_2\text{O}$ (25 g.) refluxed with gradual addn. of VII, the soln.
heated 1 hr. at 55° , kept overnight, volatile material evapd.
in vacuo, the residue distd. over 0.2 g. ethyl centralite, and the
fractions (11.3 g.), b_{0.04-0.06} $33-8^\circ$, and (1.6 g.)
b_{0.05-0.08} $32-9^\circ$, combined and redistd. yielded 36.6%
 $\text{CF}_3\text{CO}_2\text{CH}_2\text{C}(\text{O}_2\text{N})_2\text{CN}$, b_{0.15} 39° , n₂₀D 1.4045, v 2260, 1812,
1610 cm^{-1} VII (42.0 g.), 53.5 g. AlCl_3 , and 1.5 g. Cu_2Cl_2
stirred in 1 l. CHCl_3 at $18-23^\circ$ with addn. of 25.1 g.
MeCH: CHCOCl , the **mixt.** heated 5 hrs. at
 $50-60^\circ$, treated with 1.5 g. Cu_2Cl_2 , heated 7 hrs. at
 $50-60^\circ$, the cooled filtered soln. poured into 2400 ml. H_2O ,
the aq. layer washed 4 times with 150 ml. CHCl_3 , the CHCl_3 washed 4
times with 100 ml. 5% aq. NaHCO_3 , and the residue on evapn. (24.2
g.) flash distd. gave 51% product, b_{0.17} $62-4^\circ$, n₂₀D 1.4573,
redistd. to yield 47% **MeCH**: $\text{CHCO}_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{CN}$, b_{0.07-0.10}
 $59-62^\circ$, n₂₀D 1.4582, d₂₀ 1.174. KOH (1.28 g.) in 15 ml.

anhyd. MeOH treated dropwise with 2.5 g. $\text{NC(O}_2\text{N)}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Me}$ gave 1.9 g. $(\text{O}_2\text{N})_2\text{CHCH}_2\text{CH}_2\text{CO}_2\text{Me}$ K salt, m. $160-1^\circ$. The salt (11.5 g.) in 300 ml. H_2O neutralized with H_2SO_4 , the aq. layer extd. 6 times with 200 ml. Et_2O , the combined org. layers washed 5 times with 100 ml. H_2O , and the dried soln. evapd, gave 5.4 g. product, purified by redistn. to give $(\text{O}_2\text{N})_2\text{CHCH}_2\text{CH}_2\text{CO}_2\text{Me}$, b0.03 $46-7^\circ$, n_{20D} 1.4554. The corresponding Na salt (4.28 g.) in 10 ml. H_2O treated with 1.70 g. $\text{H}_2\text{C:CHCO}_2\text{Me}$ and kept 24 hrs., extd. 4 times with 50 ml. Et_2O , and the product (2.4 g., m. $43-5^\circ$) recrystd. from alc. (C) yielded 40% snowwhite $(\text{O}_2\text{N})_2\text{C}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2$, m. $45.5-6.0^\circ$. Reactions of the dinitrocyanomethide ion with org. halides gave products, which represented covalent bond formation derived from all 3 possible contributing structures $[-\text{C}(\text{CN})(\text{NO}_3)_2, \text{O}_2\text{N}(\text{CN})\text{C: N}(\text{O})\text{O}-, (\text{O}_2\text{N})_2\text{C:C:N:-}]$ of the ion. Only Me, $\text{H}_2\text{C:CHCH}_2$, and Me_3C halides gave stable isolable products. $\text{AgC}(\text{NO}_2)_2\text{CN}$ (28.7 g.) in 300 ml. MeCN heated 3 hrs. at $40-5^\circ$ with 18.0 g. $\text{H}_2\text{C:CHCH}_2\text{Br}$, filtered from 9.2 g. AgBr, the mixt. heated 4 hrs. at $40-60^\circ$ with 2 g. $\text{H}_2\text{C:CHCH}_2\text{Br}$, the filtered soln. kept 2 days with 2 g. $\text{H}_2\text{C:CHCH}_2\text{Br}$, the filtered soln. evapd., the residue taken up in Et_2O , the washed and dried soln. evapd., and the residue (10.4 g.) flash distd, gave 35% material, n_{20D} 1.4558, fractionated through a Holtzman column to give 3.5 g. pure $\text{H}_2\text{C:CHCH}_2\text{C}(\text{NO}_2)_2\text{CN}$, b0.4 $38-40^\circ$, n_{20D} 1.4552. Me_3CBr (55.0 g.) **stirred** (cooling bath) with addn. of 9.6 g. $\text{AgC}(\text{NO}_2)_2\text{CN}$, the mixt. **stirred** 2 hrs. at 20° , dild. with 200 ml. Et_2O , kept overnight, the soln. extd. 3 times with 250 ml. 5% NaOH, the Et_2O washed, dried, evapd., and the oily residue sublimed yielded 17% $\text{Me}_3\text{CC}(\text{NO}_2)_2\text{CN}$ (VIII), m. $120-4^\circ$, v 1595 cm^{-1} . The alk. ext. acidified with H_2SO_4 and the liberated amide crystd. from warm aq. MeOH yielded 18% $(\text{O}_2\text{N})_2\text{CHCONHCMe}_3$, (IX), m. $110-11^\circ$ (decompn.). II (16.4 g.) and 12.4 g. $\text{NaC}(\text{NO}_2)_2\text{CN}$ in 39.3 g. Me_3COH **stirred** 20 hrs. at 60° , the cooled mixt. dild. with Et_2O , the lower aq. layer extd. with Et_2O , the combined solns. evapd. in vacuo, the oily residue extd. with petr. ether, the insol, residue taken up in Et_2O , the ext. washed with 5% aq. NaHCO_3 , and the alk. washings acidified gave 1.2 g. material, m. $99-100^\circ$. The petr. ether ext. washed with 5% aq. NaHCO_3 and the ext. acidified gave 0.3 g. similar material, combined (9.1%) and recrystd. from dil. MeOH to give IX, in. $110.5-11.0^\circ$ (decompn.). The washed ext. concd. and cooled to -70° yielded 13.6% material, m. 120° (decompn.), recrystd. from alc. to give VIII, m. $132-3^\circ$ (decompn.). $\text{NaC}(\text{O}_2\text{N})_2\text{CN}$ (15.3 g.) in Et_2O treated dropwise with H_2SO_4 , the filtered soln. treated with 200 ml. Me_3COH and 15 g. H_2SO_4 24 hrs. at 50° , the volatile material removed, the H_2O -washed product taken up in Et_2O , the washed and dried soln. evapd., the MeOH-washed residue (11.0 g.) taken up in warm C_6H_6 , dild. with petr. ether, filtered from pptd. IX, the filtrate evapd., and the residue freed from VIII by extn.

with petr. ether gave 1.3 g. solid, m. 162-5°, recrystd. to give (O₂N)(C(CN):N(O)OCMe₃, m. 164-5°. MeI (250 g.) **stirred** 15 min. with addn. of 41.8 g. AgC(NO₂)₂CN, the mixt. **stirred** 1 hr. at 20°, dild. with 250 ml. Et₂O, and filtered after 1 hr. gave 14.9 g. O₂NC(CN):N(O)OMe (X), m. 62-4° (H₂O), identified from a study of hydrolysis products in acidic and basic solns. and by the strong ultraviolet absorption band at 300 mμ.

CC 27 (Aliphatic Compounds)

L36 ANSWER 25 OF 32 HCA COPYRIGHT 2004 ACS on STN

53:50960 Original Reference No. 53:9137g-i,9138a-b Kinetics of the reaction between a vinyl fluoride and sodium ethoxide. Silversmith, Ernest F.; Smith, Doris (Mount Holyoke Coll., South Hadley, MA). Journal of Organic Chemistry, 23, 427-30 (Unavailable) 1958. CODEN: JOCEAH. ISSN: 0022-3263.

AB Ph₂C:CHF (I), treated with NaOEt in alc. at 99.75°, was converted by an addn.-elimination reaction to Ph₂C:CHOEt (II) at a rate 270 faster than the conversion of Ph₂C:CHCl (III). BrCH₂CO₂Et (110 g.) and 129 g. anhyd. KF processed according to Bacon, et al. (C.A. 42, 8777e), and the **mixt. stirred mechanically** yielded 15.0 g. FCH₂CO₂Et (IV). Decanted PhMgBr (10.0 g. Mg and 30.0 g. PhBr in 200 ml. Et₂O) treated in 1 hr. with 6.1 g. IV in 200 ml. Et₂O with stirring at -65 ± 10° (solid CO₂Me₂CO bath) in an N atm., the mixt. **stirred** slowly at -11° with 15 g. NH₄Cl in 200 ml. H₂O, the dried (Na₂SO₄) Et₂O layer evapd., and the residue fractionated yielded 41% FCH₂CPh₂OH (V), m. 71.8-2.6°. V (1.55 g.) in 50 ml. dry C₆H₆ refluxed 2.75 hrs. with 1.59 g. P₂O₅, the decanted soln. evapd., and the residue distd. gave 0.83 g. I, b₂ 102-3°, oxidized with alk. KMnO₄ to Ph₂CO, identified through the 2,4-dinitrophenylhydrazone, m. 240°. PhMgBr (17 g. Mg and 85 g. PhBr in 150 ml. Et₂O) added dropwise with stirring at 0° to 20 g. ClCH₂CO₂Et in 200 ml. Et₂O, the mixt. dild. with 200 ml. ice-water, the H₂O-washed and dried (MgSO₄) Et₂O layer fractionated, and the distillate, b₂ 140°, recrystd. (C₆H₁₄) gave 9.0 g. ClCH₂CPh₂OH (VI), m. 63.4-5.0°. VI (6.4 g.) and 6.0 g. P₂O₅ refluxed 1 hr. in 50 ml. dry C₆H₆ and the mixt. distd. yielded 70% III, b₅ 138-9°, oxidized to Ph₂CO. For rate detns. weighed samples of I or III dild. with alc. NaOH at 25° were heated at 99.75 ± 0.05° in ampuls and the NaOEt concns. detd. periodically by titration of 5 ml. aliquots with standard HCl against phenolphthalein. I (3.0 g.) in 70 ml. 0.64M NaOEt in alc. heated 118 hrs. at 99.75°, the mixt. dild. with 500 ml. H₂O, extd. 4 times with 100 ml. Et₂O, the ext. evapd., and the residue distd. gave III, b₂ 136-8°, oxidized to Ph₂CO. The suggested addn.-elimination mechanism was discussed.

CC 10E (Organic Chemistry: Benzene Derivatives)

L36 ANSWER 26 OF 32 HCA COPYRIGHT 2004 ACS on STN

52:103947 Original Reference No. 52:18253g-i,18254a-i,18255a-e
Fluorocyclohexanes. III. cis-1H,4H-trans-2H- and
trans-1H,2H-cis-4H-Nonafluorocyclohexane and derived compds..
Godsell, J. A.; Stacey, M.; Tatlow, J. C. (Univ. Birmingham, UK).
Tetrahedron, 2, 193-202 (Unavailable) 1958. CODEN: TETRAB. ISSN:
0040-4020.

AB The nonafluorocyclohexanes (I, II), b. 92° and 101°,
were dehydrofluorinated to give the same 6 compds. identified by
oxidation and other studies as 3H,4H- and 4H,5H-
octafluorocyclohexene (III, IV), 1H-1,4-, 1H-1,3-, and
2H-1,3-heptafluorocyclohexadiene (V, VI, VII), and C₆H₆, thus
indicating a 1H,2H,4H-structure for the satd. precursors.
Fractional distn. controlled by analytical gas chromatography of the
partly fluorinated cyclohexane mixt., b. above 91.7° (C.A.
51, 3472e), gave I, b. 92.0-2.5°, m. 44-6°, a mixed
intermediate fraction, and II, b. 101°, m. 12-14°,
nD₁₄ 1.3194, in 10 and 5% yields of the original polyfluoride mixt.
I (11.0 g.) refluxed 6 hrs. with 10.0 g. KOH in 10 ml. H₂O and the
org. phase (9.0 g.) sepd., washed with H₂O and dried (MgSO₄), the
mixt. sepd. in a 16 ft. + 3 cm. tube packed with 1:2 dionyl
phthalate-kieselguhr at 80° with 10 l./hr. N flow,
and each fraction distd. in vacuo gave 0.18 g. V, b.
66.5-67°, nD₁₈ 1.3275, 1.37 g. VI (or VII), b.
71.5-2.5°, nD₁₈ 1.3400, 0.51 g. VII (or VI), b. 76°,
nD₁₈ 1.3383, 0.46 g. C₆F₆, b. 80°, nD₁₈ 1.3746, 3.75 g. III,
b. 85°, nD₁₈ 1.3277, 2.51 g. IV, b. 90°, nD₁₈ 1.3283.
The conjugated dienes VI and VII were unstable with evolution of HF
and the decompn. was retarded by storage at 0° in tightly
closed vessels. V (1-12 g.) shaken 14 hrs. in an autoclave at
20° with 10 g. KMnO₄ in 50 ml. H₂O and the mixt. heated 4
hrs. at 100°, the product isolated according to T. and
Worthington (C.A. 47, 1070c), and crystd. (Me₂CO-CHCl₃) gave 42%
dianilinium difluoromalonate, m. 161-2°, and
bis(S-benzylthiuronium) difluoromalonate, m. 184-6°. V
showed v 1723, 1770 cm.⁻¹ but no selective absorption in the range
240-300 mμ. Oxidation of VI (or VII) 17 hrs. at 100° with
aq. KMnO₄ and isolation as above gave 20% dianilinium
tetrafluorosuccinate, m. 224-5°, and bis(S-benzylthiuronium)
tetrafluorosuccinate, m. 189-90°. The diene (2.0 g.) and 1.5
g. Cl irradiated 18 hrs. with ultraviolet light in a sealed
hard-glass tube and the mixt. poured into aq. Na₂S₂O₅, the
product dried (P₂O₅), and distd. gave 2.63 g.
1,2,3,4-tetrachloroheptafluorocyclohexane, C₆HCl₄F₇, b.
197-9°. VI (or VII) gave bands at v 1682, 1743 cm.⁻¹ and
λ 254 mμ (ε 3720, alc.). Similarly, VII (or VI),
v 1679, 1732 cm.⁻¹, λ 262.5 mμ (ε 3070, alc.) was

oxidized and the product isolated as 49% dianilinium tetrafluorosuccinate, converted to the bis(S-benzylthiuronium) salt. Chlorination yielded 74% C₆HCl₄F₇, b. 184-5°. III (0.18 g., ν 1749 cm.⁻¹, no selective absorption between 240 and 300 m μ) was heated 16 hrs. at 85° with 15 g. KMnO₄ and 3 g. NaHCO₃ in 50 ml. H₂O in a rocking autoclave and the product worked up as usual to give 1.67 g. acidic solid, distd. (0.22 g.) at 160-70°/15 mm. onto a cold finger to give 0.18 g. hygroscopic DL-threo-2H,3H-hexafluoroadipic acid (VIII), m. 126-8°. The crude acid (0.29 g.) in H₂O at pH 4 treated with aq. S-benzylthiuronium chloride yielded 0.11 g. bis(S-benzylthiuronium) salt, C₂₂H₂₄F₆N₄O₄S₂, m. 226-7° (H₂O). The acid and its derivs. are unstable and attempts to prep. a dianilinium salt and a diamide failed. Chlorination of 1.97 g. III yielded 1.81 g. 1H,2H-3,4-dichlorooctafluorocyclohexane, C₆H₂Cl₂F₈, b. 143-4°. III (2.23 g.) refluxed 8 hrs. with 10 g. KOH in 10 ml. H₂O and the washed and dried (MgSO₄) org. layer sepd. (1.19 g.) by preparative scale gas chromatography yielded 0.72 g. VI (or VII), b. 72°, 0.26 g. VII (or VI), b. 76°, and 0.14 g. C₆F₆. VIII (1.0 g.) and 5.0 g. KMnO₄ refluxed 22 hrs. in 30 ml. N KOH and the sapon. product worked up yielded 73% (CF₂CO₂H)₂, m. 112-14°; dianilinium salt, m. 225-6° (Me₂CO-CHCl₃). IV (2.16 g., ν 1750 cm.⁻¹, no selective absorption in the ultraviolet) oxidized at 100° without addn. of NaHCO₃ to an acidic solid (1.21 g.) and a portion (0.44 g.) distd. at 180°/15 mm. gave 0.37 g. hygroscopic DL-3H,4H-hexafluoroadipic acid (IX), m. 150-1°; dianilinium salt, m. 186-7° (Me₂CO-CHCl₃); bis(S-benzylthiuronium) salt, m. 227-8° (H₂O). IX (0.25 g.) and 0.5 ml. HFO₃S refluxed 2 hrs. in 10 ml. alc. and the mixt. poured into H₂O, extd. with Et₂O and the filtered dried (MgSO₄) ext. satd. 30 min. with NH₃, kept 15 hrs. at 10-15°, and evapd. gave 0.08 g. diamide, C₆H₆F₆N₂O₂, m. 206-7° (H₂O). Chlorination of IV yielded 54% 1H,2H-4,5-dichlorooctafluorocyclohexane, b. 138-9°. IV (6.0 g.) refluxed 12 hrs. with 10.0 g. KOH in 10 ml. H₂O and the washed and dried product (4.26 g.) sepd. by gas chromatography gave 1.66 g. V, 0.54 g. C₆F₆, and 174 g. IV. IX (1.19 g.) refluxed 19 hrs. with 5 g. KMnO₄ and 30 ml. N KOH and worked up gave 0.95 g. acidic solid (X); dianilinium salt, m. 164-5°. X (0.69 g.) distd. at 155°/15 mm. onto a cold finger yielded 0.61 g. CF₂(CO₂H)₂, m. 115-16°. IX (5.0 g.) in 100 ml. alc. and 15.5 g. l-brucine in 200 ml. alc. boiled and the filtered soln. evapd. at 15 mm., the residue taken up in 100 ml. hot H₂O and the soln. kept 3 days at 10-15°, filtered (mother liquor A), and the residue (5.61 g.) twice recrystd. (25-35 ml. H₂O) gave 3.87 g. less sol. diastereoisomeric dibrucine salt (XI), m. 250° (decompn.), [α]_D²⁰ -12.6° (c 2.05, alc.). Mother liquor A concd. and filtered (mother liquor B) and the cryst. residue recrystd.

(H₂O) 5 times gave 1.51 g. XI. XI (51.03 g.) in 50 ml. warm H₂O made faintly alk. with 0.025 N NaOH and filtered from pptd. brucine (95% recovery), the filtrate acidified with H₂SO₄ and extd. continuously with Et₂O, and the dried (MgSO₄) ext. evapd. yielded 1.08 g. acidic solid, distd. (0.94 g.) at 220-30°/15 mm. to give 0.56 g. l-IX, $[\alpha]_{D24} -17.5^\circ$ (c 4.0, H₂O); bis(S-benzylthiuronium) salt, m. 227-8° (H₂O), $[\alpha]_{D24} -10.9^\circ$ (c 1.28, MeOH). The mother liquor B concd. and the crude salt purified to const. rotation gave 3.15 g. more sol. diastereoisomeric dibrucine salt, m. 250° (decompn.), $[\alpha]_{D21} -1.94^\circ$ (c. 2.05, alc.), neutralized (2.81 g.) to give 0.75 g. crude acid, distd. (0.60 g.) to 0.43 g. d-IX, $[\alpha]_{D22} 16.6^\circ$ (c 1.93, H₂O); bis(S-benzylthiuronium) salt, m. 227-8° (H₂O), $[\alpha]_{D24} 9.0^\circ$ (c 1.3, MeOH). II (45.0 g.) refluxed 6 hrs. with 75 g. KOH in 75 ml. H₂O and the org. layer worked up and dried gave 31.5 g. product. Preparative scale gas chromatographic sepn. of 8.94 g. mixt. and vacuum distn. of the fractions gave 0.67, 2.03, 0.69, 0.81, 0.35 and 3.90 g. of V, VI (or VII), VII (or VI), C₆F₆, III, and IV, resp. Samples (1 g.) of I and II were shaken 30 min. at 45° with 10 ml. 2N KOH in sealed tubes and the products analyzed by gas chromatography over 1:2 diononyl phthalate-kieselguhr at 77° with 1.0 l./hr. N flow and over 1:3 tricresyl phosphate-kieselguhr at 85° with 0.9 l./hr. N flow. I gave very little of the monohexenes and only traces of the dienes whereas more than 50% of II was decompd. with formation of considerable quantities of monohexenes but only small amts. of dienes. IV (5.02 g.) in 25 ml. Et₂O added dropwise in 10 min. to 0.88 g. LiAlH₄ stirred in 25 ml. Et₂O at 0° and the mixt. kept 10 min., decompd. with 25 ml. H₂O and 25 ml. 50% H₂SO₄ and the dried Et₂O evapd. through a 1 ft. gauze-spiral packed column, the residue, b. above 34°, fractionated by gas chromatography, and the fractions distd. in vacuo gave 1-63 g. 1H,trans-4H,5H-heptafluorocyclohex-1-ene (XII), b. 103-4°, n_D18 1.3503, ν 1710 cm.⁻¹ [over the range 650-3500 cm.⁻¹ identical with the spectrum of a heptafluorocyclohexene obtained by dehydrofluorination of 1H,2H,4H,5H-octafluorocyclohexane, b. 119° (cf. Stephens and T., C.A. 51, 16322b)], and 1.64 g. mixt. of 2-hexafluorocyclohexenes, b. 117-19°. XII treated 17 hrs. with aq. KMnO₄ and worked up gave 23% DL-3H,4H-hexafluoroadipate, m. 189-90°; bis(S-benzylthiuronium) salt, m. 226-7°. XII (2.92 g.) refluxed 2.5 hrs. with 4.5 g. KOH in 4.5 ml. H₂O and the H₂O-washed org. layer dried (MgSO₄) gave on preparative-scale chromatography 0.16 and 0.05 g. hexafluorocyclohexa-1,4-dienes, 0.48 g. C₆H₅F, b. 89°, and 1.15 g. XII, with identical infrared spectra with those of the 4 analogous products from the dehydrofluorination of 1H,2H,4H,5H-octafluorocyclohexane, b. 119°. Infrared spectra

of all new compds. were measured and deposited in the Documentation of Molecular Spectra, issued by Butterworths. The complete stereochemistry of I and II was suggested by the dehydrofluorinations and confirmed by further fluorination to give the known decafluorocyclohexanes showing that I and II are cis-1Ha, 4He-trans-2Ha- and trans-1Ha,2Ha-cis-4Ha-nonafluorocyclohexane, resp.

CC 10D (Organic Chemistry: Alicyclic Compounds)

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52:34749 Original Reference No. 52:6177i,6178a-i,6179a-d The dinitrogen pentoxide-olefin reaction. Stevens, Travis E.; Emmons, William D. (Rohm & Haas Co., Huntsville, AL). Journal of the American Chemical Society, 79, 6008-14 (Unavailable) 1957. CODEN: JACSAT. ISSN: 0002-7863.

AB Abs. HNO₃ (100 g.) dehydrated with P₂O₅ and the **product** sublimed in ozonized O gave 45-50 g. N₂O₅ (I) which was trapped and stored at -78°. Solns. of I were prepd. by adding the solvent to the I at -78° and warming to -10 to 0°. I (0.353 mole) in 200 cc. dry CHCl₃ added dropwise to 75 cc. cyclohexene in 100 cc. CH₂Cl₂ during 40 min. at about -30°, the mixt. kept 1 hr. at -10°, quenched with aq. NaHCO₃, and the org. layer washed, dried, and evapd. gave 60.3 g. residue; a 28.8-g. portion dissolved in 50 cc. MeOH and cooled to -78° deposited 1.96 g. bis(2-nitrosocyclohexyl nitrate), m. 149° (decompn.) (EtOHCHCl₃). Distn. of the residual mixt. gave 14-17% mixed nitrocyclohexenes, b_{0.4} 40-4°, n_{20D} 1.4821-1.4833. A 31.5-g. portion of the residue shaken with 50 cc. C₆H₆, and the C₆H₆ soln. chromatographed on silica gel yielded some pure cis- and trans-isomer of 2-nitrocyclohexyl nitrate (II). Oily nitronitrates (3.7 g.) from the cyclohexene-I reaction passed with C₆H₆ through silica gel, shaken with 100 cc. 5% aq. NaOH, kept overnight, the basic soln. decanted from insol. oil, added dropwise to excess cold 15% H₂SO₄, and the Et₂O evapd. gave 1.4 g. residue yielding with an equal amt. of 2,4-(O₂N)₂C₆H₃NHNH₂ 2.02 g. solid deriv.; a 1.09-g. portion chromatographed on silica gel yielded 0.47 g. cyclohexenone deriv., m. 164-5°, and 0.35 g. 4-nitratocyclohexanone deriv., m. 150-1°. Mixed cis- and trans-II gave similarly 1.2 g. 2,4-dinitrophenylhydrazones from which no pure compd. could be isolated. I (0.100 mole) in 80 cc. CH₂Cl₂ added during 20 min. to 15 cc. cyclohexene and 19.2 g. Et₄NNO₃ (III) in 200 cc. CH₂Cl₂ at -20°, warmed to 0°, **stirred** 0.5 hr., quenched with aq. NaHCO₃, and the org. layer worked up gave 7.8 g. 3-nitrocyclohexene, b_{0.5} 50-2°, n_{20D} 1.4837, b₅ 68°, n_{20D} 1.4828, and 4.1 g. cis-II, b_{0.5} 130°, n_{20D} 1.4834, m. 32-3°. I (0.149 mole) in 100 cc. CH₂Cl₂ added slowly with stirring to 15 cc. C₃H₆ in 300 cc. CH₂Cl₂ at -20 to -30°, warmed to 0°, **stirred**

15 min., quenched with aq. NaHCO_3 , and the org. layer concd. in vacuo to 100 cc. and chromatographed on silica gel gave 2.1 g. **mixt.** of MeCH:CHNO_2 (IV) and $\text{CH}_2\text{:CHCH}_2\text{NO}_2$ (V), b₂₀ 36-40°, n_{20D} 1.4338, 0.8 g. intermediate fraction, and 6.0 g. $\text{O}_2\text{NCH}_2\text{CH(ONO}_2\text{)Me}$ (VI), b_{0.3} 60°, n_{20D} 1.4461, also obtained, b_{0.1} 50°, n_{20D} 1.4462, from $\text{MeCH(OH)CH}_2\text{NO}_2$ and I. I (0.135 mole) added to excess C_3H_6 in 300 cc. CH_2Cl_2 contg. 28.8 g. III gave 1.4 g. nitroolefins, n_{20D} 1.4326, 0.6 g. intermediate fraction, and 6.9 g. VI, n_{20D} 1.4454. A similar run with 0.150 mole I, excess C_3H_6 , and 19.2 g. III during 1 hr. at 0° yielded 2.9 g. nitroolefin, b₄₀ 76-8°, n_{20D} 1.4334, and 1.5 g. trap residue, n_{20D} 1.4306, contg. 0.3 g. IV and 0.7 g. V; the nitroolefin fraction consisted of 2.0 g. V and 0.5 g. IV; further distn. of the crude product gave 11.8 g. VI, n_{20D} 1.4453. The aq. and NaHCO_3 washes neutralized with dil. HCl and extd. with Et₂O gave 1.2 g. residue not investigated further. $\text{MeCH(OH)CH}_2\text{NO}_2$ dehydrated with $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ gave IV, b₃₇ 58°, n_{20D} 1.4545. I (0.120 mole) and excess EtCH:CH₂ gave 1.4 g. nitrobutenes, b₅ 34-6°, n_{20D} 1.4398, and 5.6 g. EtCH(ONO)₂CH₂NO₂ (VII), b_{0.4} 60-2°, n_{20D} 1.4467. I (0.097 mole) and excess EtCH:CH₂ contg. 20.0 g. III gave 1.4 g. nitrobutenes, n_{20D} 1.4404, and 4.2 g. VII, n_{20D} 1.4470; redistn. of the nitrobutene fraction gave $\text{MeCH:CHCH}_2\text{NO}_2$ (VIII), b₅₃ 75°, n_{20D} 1.4389. A similar run with 0.160 mole I and excess EtCH:CH₂ during 1 hr. at 0° gave 3.8 g. forerun, b₅ 36-8°, n_{20D} 1.4400, 1.0 g. intermediate cut, and 13.5 g. VII, b_{0.2} 62°, n_{20D} 1.4466; the forerun consisted of 2.85 g. VIII and 0.25 g. EtCH:CHNO₂. EtCH(OH)CH₂NO₂ dehydrated with $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ gave VIII, b₃₇ 72°, n_{20D} 1.4563. I (0.150 mole) and 30 cc. Me₂C:CH₂ in 250 cc. CH_2Cl_2 contg. 20.0 g. III gave 5.3 g. $\text{O}_2\text{NCH}_2\text{CMe:CH}_2$, b₃₀ 52-4°, n_{20D} 1.4434, 1.7 g. intercut, and 7.9 g. Me₂C(ONO₂)CH₂NO₂, b_{0.4} 62-4°, n_{20D} 1.4500, also obtained, b_{0.4} 60°, n_{20D} 1.4487, from $\text{O}_2\text{NCH}_2\text{C(OH)Me}_2$ and I. I (0.090 mole) in 66 cc. CH_2Cl_2 added with stirring to 10.0 g. III and 15 cc. trans-(MeCH:)₂ in 100 cc. CH_2Cl_2 gave 1.9 g. mixed nitroolefins, and 7.1 g. threo-MeCH(NO₂)CH(ONO₂)Me (IX), b_{1.5} 63°, n_{20D} 1.4436. I (0.090 g.) and 15 cc. cis-(MeCH:)₂ gave similarly 7.2 g. erythro isomer of IX, b_{1.5} 60°, n_{20D} 1.4462. PhCH₂CH:CH₂ and I gave a product showing no nitrate ester absorption; a 5.00-g. portion of the residue oxidized with H₂SO₄-Na₂Cr₂O₇, gave 0.96 g. p-O₂NC₆H₄CO₂H, m. 230-2°. 1-Octene (10.9 cc.) and 6.2 cc. C₆H₆ in 125 cc. CH_2Cl_2 treated dropwise during 25 min. with 0.050 mole I in 34 cc. CH_2Cl_2 at -5°, **stirred** 15 min. at 0°, quenched with aq. NaHCO_3 , and the org. layer worked up gave a residue contg. 1.6 g. PhNO₂. A similar run, but in the presence of 9.6 g. III, gave 10.0 g. residue contg. 0.17 g. PhNO₂. threo-IX (1.50 g.), 0.15 g. PtO₂, and 10 cc. AcOH hydrogenated at room temp. and 3 atm. during 24 hrs., filtered, evapd., and the residue kept

overnight with 5 cc. pyridine and 4 cc. Ac₂O, evapd., dissolved in 9:1 CH₂Cl₂-EtOAc, and chromatographed on silica gel gave 1.28 g. dl-threo-MeCH(OAc)CH(NHAc)Me(X), m. 71-2.5° (C₆H₆-ligroine). erythro-IX (1.50 g.) gave similarly 1.45 g. (crude) dl-erythro-isomer of X, m. 50-2°. cis-II (2.00 g.) and 0.20 g. PtO₂ in 10 cc. AcOH hydrogenated 4 hrs. at room temp. and 3 atm., filtered, evapd., and the residue treated with 25 cc. 6N HCl, evapd. in vacuo, dild. with 30 cc. C₆H₆, distd. to dryness, and recrystd. from C₆H₆-EtOH gave 0.70 g. cis isomer of 2-aminocyclohexanol (XI).-HCl, m. 184-5° (decompn.) (EtOH-C₆H₆); N-Bz deriv. of XI, m. 183-4°. The nitro alc. fraction from cyclohexene and I refrigerated slowly deposited trans-2-nitrocyclohexanol (XII), m. 46-7°. Iso-Pr₂NH.HNO₂ (17.8 g.) and 9.8 g. cyclohexene oxide in 75 cc. Me₂SO **stirred** 18 hrs. at 65°, poured into H₂O, extd. with Et₂O, and the ext. worked up gave 3.3 g. XII, n₂₀D 1.4837. XII (2.00 g.) hydrogenated in the usual manner gave 0.93 g. trans-XI.HCl, m. 174-5° (C₆H₆-EtOH). Cl(CH₂)₂CH(OH)Me (XIII) (16.4 g.), n₂₀D 1.4430, and 29.0 g. NaI in 175 abs. EtOH refluxed 4 hrs., poured into H₂O, extd. with Et₂O, and the ext. worked up gave 6.6 g. unchanged XIII, b₂₀ 75-80°, n₂₀D 1.4435, and 14.4 g. (crude) I(CH₂)₂CH(OH)Me (XIV), b₁₀ 76°, n₂₀D 1.5343. XIV (14.6 g.) and 16.5 g. AgONO yielded 5.6 g. O₂N(CH₂)₂CH(OH)Me (XV), b_{0.2} 49°, n₂₀D 1.4445. XV (4.3 g.) in 70 cc. CH₂Cl₂ treated at -30° with 0.042 mole N₂O₅ in CH₂Cl₂, warmed to 0°, and worked up in the usual manner gave 3.3 g. MeCH(ONO₂)(CH₂)₂NO₂, b_{0.2} 66°, n₂₀D 1.4522.

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51:81397 Original Reference No. 51:14689h-i,14690a-f Acetylenic compounds. LV. The preparation and properties of some polyacetylenic acids, and their derivatives. Jones, E. R. H.; Thompson, J. M.; Whiting, M. C. (Univ. Manchester, UK). Journal of the Chemical Society, Abstracts 2012-17 (Unavailable) 1957. CODEN: JCSAAZ. ISSN: 0590-9791. OTHER SOURCES: CASREACT 51:81397.

AB cf. C.A. 51, 6507e. 1,3-Heptadiyne (17.5 g.) (sic) in 35 cc. Et₂O was added dropwise to EtMgBr (from 10 g. Mg) in Et₂O, refluxed 1 hr., poured onto excess CO₂ in an autoclave, and the complex decompd. with ice and 15% H₂SO₄ to give 13.5 g. 2,4-heptadiynoic acid, m. 73-5° (from light petroleum, b. 40-60°); Me ester (from CH₂N₂ or H₂SO₄ in MeOH), b_{0.01} 50°, n_D17.5 1.5131. Similarly was prepd. from 1,3-octadiyne, 40% 2,4-nonadiynoic acid, m. 32-7° (from pentane). 1,4-Dichloro-2-butyne (74 g.) was added with stirring to a suspension of NaNH₂ in liquid NH₃, Et₂O and dried paraformaldehyde in Et₂O added, after 1 hr. NH₄Cl added, the NH₃ evapd., the soln. filtered, the solid washed with Et₂O, the filtrate and washings evapd. and dried, the residue extd. with light petroleum (b.

40-60°), and the ext. evapd. at 0.01 mm. at room temp. to give 47 g. red oil, n_{D20} 1.521-1.522, which solidified, identified as 2,4-pentadiyn-1-ol (I). Distn. of this is hazardous. I (21 g.) in 170 cc. C₆H₆ was added with cooling to EtMgBr (from 17 g. Mg) in C₆H₆, after 40 min., 18 g. MeCHO added, the mixt. stirred 18 hrs., the complex decompd. with ice H₂O, the C₆H₆ layer sepd. and the aq. layer continuously extd. with C₆H₆, the exts. dried and evapd., the residue dissolved in C₆H₆, and adsorbed on alumina giving 33% 2,4-heptadiyne-1,6-diol (II), b. 85° (bath temp.)/5 + 10-4 mm., m. 50-3° (from Et₂O). Similarly, from I and EtCHO was prepd. 56% 2,4-octadiyne-1,6-diol (III), b. 0.02 100° (bath temp.), n_{D21} 1.5370, λ 2310 A., ϵ 1050. II and pyridine treated with SOCl₂ gave 35% dichloride (IV), b. 0.01 31°, n_{D19} 1.5530, λ 2670, 2520, 2390, 2270 A., ϵ 1350, 2050, 1650, 1100. III treated likewise gave the dichloro compd. (V), b. 0.01 60°, n_{D23} 1.5457, λ 2670, 2520, 2390, 2260 A., ϵ 1450, 2250, 1850, 1450 (plus 30% 1-chloro-6-octene-2,4-diyne, $n_{D19.5}$ 1.5703, λ 2890, 2830, 2730, 2650, 2540, 2535, 2400 A., $E_{1cm.1\%}$ 320, 370, 500, 510, 380, 400, 260). V in Et₂O was added during 10 min. to a suspension of NaNH₂ in liquid NH₃ cooled to -77° by addn. of liquid N, NH₄Cl added, the soln. extd. with isobutane, the ext. evapd. in the presence of MgSO₄, tetrahydrofuran added, and the soln. added to EtMgBr. Carbonation and purification gave 10% 2,4,6-nonatriynoic acid, decomp. 95° (from CH₂Cl₂). IV was similarly dehydrohalogenated and added to EtMgBr to give octa-2,4,6-triynoic acid monohydrate; Me ester, m. 53-6° (from light petroleum). Me hepta-2,4-diynoate (VI) and NH₃ soln. were shaken 3.5 hrs. at 15° to yield 2,4-heptadiynamide (VII), m. 148° (from C₆H₆-EtOH). Me 2,4,6-octatriynoate likewise gave 2,4,6-octatriynamide, discolored at 85° (from tetrahydrofuran-CH₂Cl₂). VII (1.0 g.), sand, and P₂O₅ was heated at 100-30°/0.01 mm. in a sublimation app. and the sublimate dissolved in C₅H₁₂ to give 400 mg. 2,4-heptadiynonitrile, m. -5°, n_{D22} 1.5387. VI formed several adducts: with CH₂N₂ it gave Me 4-but-1-ynylpyrazole-3-carboxylate, m. 92-4° (from C₆H₆-light petroleum), λ 2405, inflections at 2435, 2615 A., ϵ 10,600, 10,400, 6600, ν 3200-3400, 1727, 2250 cm.⁻¹; with piperidine VI gave Me 3-(1-piperidyl)hept-2-en-4-ynoate, b. 140° (bath temp.)/10-4 mm., n_{D17} 1.5551, λ 2320, 3090 A., ϵ 6700 and 14,700, ν 2247, 1706, 1630 cm.⁻¹; and with cyclopentadiene, Me 2,5-dihydro-2,5-endomethylene-6-but-1-ynylbenzoate, b. 0.01 71° (bath temp.), n_{D23} 1.5335, λ 2915 A., ϵ 6220, ν 3070, 2245, 2215, 1707, 720 cm.⁻¹ Ultraviolet absorption data are given for RC.tplbond.CC.tplbond.CCOX (R and X given): Et, OH; Bu, OH; Et, OMe; Et, NH₂; Me₂C(OH), OH. For R(C.tplbond.C)3COX: Me, OH; Et, OH; Me, OMe; Et, OMe; Me, NH₂. For EtC.tplbond.CCN, Et(C.tplbond.C)2CN, and Et(C.tplbond.C)3CN.

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51:81209 Original Reference No. 51:14601c-i,14602a-g Nitrosoacylamines and diazo esters. XII. Carbonium rearrangement in the decomposition of alkyl diazo esters. Huisgen, Rolf; Ruchardt, Christoph (Univ. Munich, Germany). Ann., 601, 1-21 (Unavailable) 1956. OTHER SOURCES: CASREACT 51:81209.

AB cf. C.A. 49, 12335i. Reactions of primary alkyl amines with HNO₂ with decompn. of the alkyl diazonium ion undoubtedly take place through the carbonium ion, the H shift leading from the primary to the secondary or tertiary alkyl group, in direct competition with the attack of the nucleophilic solvent. The extent of such isomerization in the decompn. of the alkyl diazonium ion within an ion-pair in a nonpolar solvent is difficult to predict. The concept of such oriented ion-pairs as intermediates *ibid.* 599, 183(1956)) offers a satisfactory explanation of the decompn. of covalent diazo esters and of the reaction of diazoalkanes with a carboxylic acid. The decompn. of alkyl diazonium ions in aq. media serves as a good approximation to the extreme case of carbonium substitution reactions, independent of the nature of the alkyl group. PrN(NO)Bz (I) (10.0 g.) in 100 cc. dry C₆H₆ heated to 55° with evolution of 60 millimoles N and MeCH:CH₂, the **mixt.** treated with ice-cold NaOH, filtered, and worked up gave 77% ProBz, b₁₁ 107°, together with 1.5 ± 0.3% iso-ProBz (by infrared detn.). Similar decompn. of 20 g. I in 200 cc. MeCN at 55° yielded 62% ProBz contg. 3.4 ± 0.6% iso-ProBz. I (14.0 g.) in 40 cc. HCONMe₂ added dropwise in 30 min. with vigorous stirring to 40 cc. H₂O and 20 cc. HCONMe₂ at 80° and worked up gave 9% ProBz contg. 9% iso-ProBz together with 46% ProH contg. 32.7% iso-ProH. The % yield of iso-ProH rises with the increasing polarity of the solvent. EtCHN₂ (II) (cf. Adamson and Kenner, C.A. 32, 1098) at 0°/350-400 mm. bubbled in N atm. through 4 cc. 70% HClO₄ in 18 cc. H₂O and 30 cc. HCONMe₂, and the products worked up gave 16.0 millimoles ProH contg. 28.1% iso-ProH. Similarly, II at 0°/400 mm. was bubbled through 30 cc. HCONMe₂, 20 cc. H₂O, and 6 g. BzOH and gave 9.3 millimoles ProH contg. 27.2% iso-ProH together with 1.1 millimoles ProBz contg. about 4.3% iso-ProBz. PrNH₂ (4.1 g.) in 14 cc. 70% HClO₄, 18 cc. H₂O, and 60 cc. HCONMe₂ **stirred** 3 hrs. with dropwise addn. of 10 g. NaNO₂ in 15 cc. H₂O at 0° and worked up gave 23.3 millimoles ProH contg. 30.8% iso-ProH. The agreement in the yields of isomers supports the conception of a common intermediate for the 3 types of reaction. The occurrence of BzOPr in addn. to ProH in the expts. in aq. media is attributed to the formation of an oriented alkyl diazonium ion-pair and a scheme summarizing the reactions in nonpolar and aq. media is given. PrNH₂ (20.0 g.) in 200 cc. AcOH **stirred** 90 min. at 0° with portionwise

addn. of 69 g. powd. NaNO_2 , the mixt. **stirred** 3 hrs. at 0° and 3 hrs. at 20° , the mixt. distd., the distillate (150 cc.) dild. with 300 cc. H_2O and distd., the org. phase sepd. and the neutralized aq. phase satd. with NaCl at 0° , extd. 3 times with 10 cc. Et_2O , the org. solns. combined and washed with NaHCO_3 , dried over CaCl_2 and distd. yielded 17.8 g. PrOAc contg. 32% iso- PrOAc . PrN(NO)Ac (27 g.) in 200 cc. AcOH decompd. by heating at 70° yielded 6.1 g. PrOAc contg. 40% iso- PrOAc . II at $0^\circ/200$ mm. passed into 35 cc. AcOH and 2 cc. Ac_2O produced 2.3 g. esters contg. 33% iso- PrOAc . These reactions apparently all take place by formation of PrNN ion and its consequent decompn. The effects of solvation and of orientation on the alkyl diazonium ion-pairs and the consequent restriction of alkyl isomerization are discussed. $\text{MeC}_6\text{H}_4\text{SO}_2\text{Pr}$ (cf. Gilman and Beaber, C.A. 19, 977) in 150 cc. pure AcOH refluxed 13 days at 120° , the PrOAc distd. with AcOH , and after diln. with H_2O azeotropically distd. yielded 8.2 g. PrOAc contg. 2.5-3% iso- PrOAc . II in Et_2O at 0° **stirred** with dropwise addn. of dry $\text{Cl}_3\text{CCO}_2\text{H}$ in Et_2O , the washed and dried mixt. evapd., and the product distd. gave $\text{Cl}_3\text{CCO}_2\text{Pr}$, b₁₂ $64-9^\circ$, contg. $1.1 \pm 0.3\%$ iso- $\text{PrO}_2\text{CCCCl}_3$. In the decompn. of $\text{Ph}_2\text{CHCHN}_2$ (III) in nonpolar solvents the Ph shift predominates. Ph_2CHCN (30 g.) in 250 cc. Et_2O added dropwise in 1 hr. to 0.18 mole LiAlH_4 in 380 cc. abs. Et_2O , the mixt. refluxed 4 hrs. and treated cautiously with 6 cc. H_2O , 4.5 cc. 20% NaOH , and 20 cc. H_2O , filtered and the residue digested with 100 cc. Et_2O , the combined Et_2O solns. dried and satd. with dry HCl , the pptd. chloride (27.0 g.) converted to the free amine, and crystd. from Ac_2O gave prismatic $\text{Ph}_2\text{CHCH}_2\text{NHAc}$, m. 89° , transformed to $\text{Ph}_2\text{CHCH}_2\text{N(NO)Ac}$ (IV), m. $42-4^\circ$, converted by stirring in abs. EtOH at -10° with NaOEt to $\text{Ph}_2\text{CHCHN}_2$ (V). IV (5.5 g.) in 90 cc. xylene slowly heated at $120-5^\circ$ liberated 18.5 millimoles N and evapd. in vacuo gave 0.68 g. PhCH:CHPh (VI), m. $123.5-4.5^\circ$ (from EtOH), and 3.35 g. α,β -diphenylethyl acetate (VII). Sapon. of VI with 1.6 g. KOH in 35 cc. boiling MeOH , crystn. of the neutral portion from alc. to yield 0.10 g. VI, and addn. of H_2O to the warm alc. mother liquor gave 2.1 g. $\text{Ph(PhCH}_2\text{)CHOH}$ (VIII), m. 66° (from petr. ether). On the basis of the yield of N, the decompn. of IV yielded 23% VI and 57% VIII. The infrared analysis of the crude product from another decompn. showed yields of 14% VI and 72% VII. IV (6.0 g.) in xylene **stirred** 20 min. in 40 cc. 0.1 mole KOEt in xylene at 0° , the mixt. washed with ice H_2O , dried over KOH and filtered, the dark red soln. decompd. at 90° with 10 cc. AcOH in 40 cc. xylene with evolution of 10 millimoles N in 20 min., and the product worked up gave 12% VI and 60% VII on the basis of 10 millimoles IV. The C_6H_6 soln. of V (from IV as above) decompd. by portionwise addn. of BzOH in C_6H_6 at 20° and the cryst. crude product (4.3 g.) fractionally crystd. from EtOH and MeOH yielded

0.18 g. VI and 1.50 g. α,β -diphenylethyl benzoate, m. 69-71°. Ph(p-MeOC₆H₄)CHCN reduced with LiAlH₄ gave 68% amine HCl salt, m. 182-4°, converted by Ac₂O to Ph(p-MeOC₆H₄)CHCH₂NHAc, m. 111°, and nitrosated to the nitroso compd. (IX), was dried over P₂O₅ to give 97% pure material. IX (8.0 g.) heated 2 hrs. at 105-10° in 200 cc. tech. pseudocumene with evolution of 24 millimoles N, the solvent evapd. at 12 mm., the residue (7.0 g.) taken up in MeOH, and refrigerated gave 0.60 g. p-MeOC₆H₄CH:CHPh; the mother liquor evapd., and the red oily residue in C₆H₁₂ chromatographed over Al₂O₃ gave 6.1 g. orange mixt. of esters contg. 3.14 g. p-MeOC₆H₄CH₂CHPhOAc (X) and 2.47 g. p-MeOC₆H₄CH(CH₂Ph)OAc (XI) (by infrared analysis). The decompn. of IX yielded 45% X, 35% XI, and 11% p-MeOC₆H₄CH:CHPh. This relative shift of p-MeOC₆H₄ and Ph in the ratio 13:10 leads to the conclusion that an energy-rich carbonium ion and not a phenonium ion (cf. Winstein, et al., C.A. 48, 2647f) is intermediate in the decompn.

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49:15976 Original Reference No. 49:3137a-i,3138a-i,3139a-i,3140a-i,3141a-i,3142a-i,3143a-i,3144a-i,3145a-i,3146a-i,3147a-i,3148a-i,3149a-i,3150a-i,3151a-b Oxazoles and oxazolones. Cornforth, J. W.; Clarke, H. T.; et al. (Oxford Univ.; Princeton Univ. Press). Chemistry of Penicillin 688-848 (Unavailable) 1949.

GI For diagram(s), see printed CA Issue.

AB OXAZOLE SECTION: New methods for constructing the oxazole ring have been devised and the behavior of functional groups elucidated. The synthesis of oxazoles and imidazoles from K β -hydroxy- α -(α -alkoxyalkylideneamino)acrylates is given. A mixt. of 51.1 g. AmCN and 24.5 g. EtOH was kept with 19.2 g. dry HCl below 0° for 2 wk, decompd. with 74 g. K₂CO₃ in Et₂O and distd. The crude AmC(OEt):NH (62.4 g.), b₁₁ 52-65°, was shaken with cold aq. H₂NCH₂CO₂Et.HCl for 1 h. The upper layer was fractionated to yield Et α -ethoxycaprylideneaminoacetate (I), b_{0.5} 91°, sapond. on gentle warming to AmCO₂Et. The corresponding Me α -methoxycaprylideneaminoacetate (Ia), b_{0.1} 74°, was similarly prepd. A soln. of 0.85 g. K in 2.5 g. EtOH and 14 g. Et₂O was dild. to 50 mL. with Et₂O, cooled to -15° and treated with a similarly cooled mixt. of 4.85 g. I and 3.2 g. HCO₂Et, yielding after 3 h. at -10°, 2.6 g. of hygroscopic needles of C₅H₁₁C(OEt):NC(CO₂Et):CHOK (II). The corresponding K Me β -hydroxy- α -(α -methoxycaprylideneamino) acrylate (IIa) was obtained in 3.2 g.-yield from 3.75 g. Ia. Treatment of 2.6 g. II and 1.25 g. DL-penicillamine in 5 cc. EtOH with alc.-HCl gave cryst. DL-N-caproylpenicillamine, m. 137-8°. Treatment of II with ethereal HCl produced Et 2-amyloxazole-4-carboxylate, b_{0.07} 99° (dinitrophenyl-hydrazone, m. 165-6°; amide,

m. 152°) sapond. to 2-amylloxazole-4-carboxylic acid, m. 92-3° (PhNH₂ salt. m. 98.5-9.5°) readily decarboxylated to 2-amylloxazole, b. 172-3°; picrate, m. 84.5-5.5°. This general synthesis of 2-substituted oxazoles and their 4-carboxylic acids has been extended to Et 2-phenyloxazole-4-carboxylate, m. 69-70°, the corresponding acid, m. 209°, and carried through to the known 2-phenyloxazole. The method can be also applied to the synthesis of imidazoles. Treatment of I with aq. NH₄OH gave 2-amylimidazole-4-carboxylic acid, m. 230° (decompn.); with MeNH₂.HCl or alc. H₂NCH₂CO₂Et.HCl, I produced, resp., Et 2-amyl-1-methylimidazole-4-carboxylate (III), m. 42-3°, and Et 2-amylimidazole-4-carboxylate-1-acetate (IIIa), m. 61°. Similarly, Ia gave Me 2-amyl-1-methylimidazole, m. 66.7°, and Me 2-amylimidazole-4-carboxylate-1-acetate, m. 107°. Hydrolysis of III and IIIa yielded 1-methyl-2-amylimidazole-4-carboxylic acid, m. 121-3°, and 2-amyl-4-carboxyimidazole-1-acetic acid, m. 132-4°. Starting from PhCH₂CN, Et 2-benzylimidazole-4-carboxylate-1-acetate, m. 111-2°, was likewise prepd., converted by treating with MeOH into a Me Et ester. On heating with aq. NH₄OH and with PhNH₂, 2-amylloxazole-4-carboxylic acid was converted into 2-amylimidazole, m. 33-4° and 1-phenyl-2-amylimidazole, m. 143-4°. Synthesis of oxazoles by rearrangement of oxazolones. The Na salt of 2-benzyl-4-hydroxymethylene-5-oxazolone (2.7 g.) in 50 mL. abs. MeOH was treated with 5 mL. abs. Et₂O contg. 0.38 g. HCl. The gummy product (2.28 g.) was taken up in 10 mL. abs. MeOH and heated for 30 min. with 6.2 mL. H₂O contg. 0.42 g. NaOH. The residue on evapn. was dissolved in 10 mL. of iced H₂O, acidified with dil. HCl to pH 6.5 and extd. with Et₂O, yielding 700 mg. 2-benzylloxazole-4-carboxylic acid, m. 158°. On heating at 220°, crude 2-phenyl-4-(α -hydroxyethylidene)-5-oxazolone rearranged to 2-phenyl-5-methyloxazole (IV), m. 184-5° (decompn.). Similarly, on heating to 230°, Na 4-hydroxymethylene-g-amyl-5-oxazolone rearranged to 2-amylloxazole-4-carboxylic acid. Evapn. of 2-(1-pentenyl)-4-(hydroxymethylene)-5-oxazolone in NaOH and fusion of the residue at 250° under reduced pressure yielded 2-pentenyl-oxazole-4-carboxylic acid, m. 145-7°. Incidental syntheses of oxazole derivs. The action of PhSO₃Ag on Me thiobenzylpenaldate di-Et acetal produced colorless prisms of 2-benzylloxazole-4-carboxylic acid, m. 156-7° and the dehydration of Et α -benzylamino-acetoacetate gave Et 2-phenyl-5-methyloxazole-4-carboxylate, m. 51-2°, hydrolyzed to the acid, m. 180-1°, decarboxylated at 220° in the presence of a trace of CuO to IV. Thus a reaction known to succeed with α -acylamino ketones and carboxylic esters is extended to β -keto esters. The 2-substituted oxazoles and their 4-carboxylic acids and esters are feebly basic, readily oxidized by

cold aq. KMnO_4 but stable to Br in CCl_4 . The ring opens on warming with 2,4-(O_2N) $_2$ - $\text{C}_6\text{H}_3\text{NHNH}_2$ in 2N HCl with a tendency to formation of glyoxal osazone derivs. Rosenmund redn. of 2-amylloxazole-4-carboxylic acid chloride produced 2-amylloxazole-4-carboxaldehyde, b8 108° (2,4-dinitrophenylhydrazone, m. 172-3°), converted by warming with D-penicillamine-HCl in AcOH to the thiazolidine, devoid of antibiotic properties. From the corresponding Et ester, 2-benzyl-4-carboxyoxazole hydrazide, m. 81-3° and benzylamide, m. 121-2° were prepd. In attempts to synthesize the thiazolidine-oxazolone structure for penicillin, attention was directed to the prepn. of 5-alkoxyoxazoles and many variations of the general method of dehydrating α -acylamino esters with **P205** were introduced. By the use of PCl_5 , **P205**, POCl_3 , SOCl_2 , and PhSO_2Cl , the following new oxazoles were prepd. (substituent given): 2-Ph, 5-MeO, b9 141°; 2-Ph, 5- PhCH_2O , m. 56°; 2- PhCH_2 , 5-EtO, b15 152-4°; 2- PhCH_2 , 5-MeO, m. 31-2°; 2-Am, 5-EtO, b0.8 82-5°; 2-Am, 5-MeO, b1.0 60-65°; 2-(1-C $_5$ H $_9$), 5-EtO, b20 125-8° (C $_5$ H $_9$ = pentenyl); 2-(1-C $_5$ H $_9$), 5-MeO, b15 108-10°; 2- PhCH:CH , 5-EtO, m. 35°; 2- PhCH:CH , 5- PhCH_2O , picrate, m. 135° (decompn.); 2-Ph, 4-Me, 5-EtO, b10 151°; 2-Ph, 4-Me, 5- PhCH_2O , picrate, m. 112-13°; 2- PhCH_2 , 4-Me, 5-EtO, b15 145-50°; 2-Am, 4-Me, 5-EtO, b3 92°; 2,4- Ph_2 , 5-EtO, m. 47-8°; 2-Ph, 4- PhCH_2 , 5-EtO, picrate, m. 105°; 2-Ph, 4- PhCH_2 , 5- PhCH_2O , picrate, m. 117°; 2,4-(PhCH_2) $_2$, 5-EtO, b0.3 145-50°; 2-Am, 4- PhCH:CH , 5-EtO, m. 92°; 2-Ph, 4-CO $_2$ Et, 5-EtO, m. 75°; 2-Am, 4-CO $_2$ Et, 5-EtO, b0.1 122-5°; 2-(1-C $_5$ H $_9$), 4-CO $_2$ Et, 5-EtO, b0.2 125°; 2- PhCH_2 , 4-CO $_2$ Et, 5-EtO, b0.1 165°. The possibility of converting an alkoxyoxazole to the corresponding oxazolone was realized by the catalytic hydrogenation of 2 g. of 2-phenyl-5-benzoyloxyoxazole in 30 mL. dry dioxane in the presence of Pd-black to 2-phenyl-5-oxazolone, m. 91°. The converse reaction, transformation of an oxazolone to an alkoxyoxazole, has also been achieved. Methylation of 3 g. of 2-phenyl-4-carbethoxy-5-oxazolone with 500 mg. CH_2N_2 in 50 mL. Et $_2$ O yielded 2-phenyl-4-carbethoxy-5-methoxyoxazole, m. 72°. Similarly, methylation of 2-phenyl-4-carbomethoxy-2-oxazolin-5-one gave 2-phenyl-4-carbomethoxy-5-methoxyoxazole, m. 98°, identical with that prepd. by the dehydration of $\text{BzNHCH}(\text{CO}_2\text{Me})_2$ with PCl_5 in CCl_4 . Attempts to obtain 5-alkoxyoxazole-4-carboxaldehydes covered a wide range. Formylation of $\text{BzNHCH}_2\text{CO}_2\text{Et}$ and condensation with PhCH_2NH_2 in Et $_2$ O gave Et β -benzylamino- α -benzamidoacrylate, $\text{R}'\text{NHCH:C}(\text{CO}_2\text{Et})\text{NHCOR}$ (V; R = Ph, R' = PhCH_2), m. 108°, cyclized by PBr $_3$, POCl_3 or PCl_5 to 2-phenyl-4-benzylaminomethylene-5-oxazolone (VI), m. 134-7; Ac deriv., m. 140°. In the same way, Et β -benzylamino- α -phenylacetamido acrylate (VIa) with PBr $_3$ gave 2-benzyl-4-

benzylaminomethylene-5-oxazolone (VIb). Dehydration of Et α -benzamido- β,β -diethoxypropionate with $\text{PCl}_5\text{-POCl}_3$ yielded 2-phenyl-4-(ethoxymethylene)5-oxazolone (VII). Distn. of benzyl α -benzamido- β,β -diethoxypropionate gave a mixt. of products including benzyl α -benzamido- β -ethoxyacrylate, m. $108-10^\circ$; benzyl 2-phenyloxazole-4-carboxylate, m. $106-7^\circ$; and VII. Attempts were made to cyclize α -benzyl- β -methyl-DL-phenylpenicilloate, $\text{HN.CH(CO}_2\text{R')}. \text{CMe}_2\text{.S.CHCH(NHCOR)CO}_2\text{CH}_2\text{Ph}$ (VIII, $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$) (VIIIa), m. 130° ; dibenzyl-DL-phenylpenicilloate (VIII, $\text{R} = \text{Ph}$, $\text{R}' = \text{PhCH}_2$) (VIIIb), m. $107-8^\circ$; and DL-2-(carboxy-1-hexenoylaminoethyl)-5,5-dimethyl-4-carbomethoxythiazolidine benzyl ester (VIII, $\text{R} = 1\text{-pentenyl}$, $\text{R}' = \text{Me}$). (VIIIc). The action of PCl_5 on VIII and VIIa gave definite evidence of formation of thiazolidinylalkoxyoxazoles and cyclization of VIIIb and chromatog. purifn. of the product gave benzyl 2-(2-phenyl-5-benzyloxy-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylate, m. $120-5^\circ$, absorption band at 2850 A . This reduced in EtOAc using a Pd-BaSO_4 catalyst with 2 mol H, corresponding to removal of 2 PhCH_2 groups, yielded a product with no-antibiotic activity. The simpler thiazolidines were also investigated. The reaction of 3-methyl-2-(benzamidocarbethoxymethyl)-thiazolidine with PCl_5 gave a Cl-contg. product, converted by NaHCO_3 to a probable sulfoxide. With PCl_3 , a product was obtained, which was converted by aq. KOH to 2-phenyl-4-hydroxymethylene-5-oxazolone. β -Methylaminoethyl mercaptan-HI (from 15 g. of 2-methylthiazoline-MeI) in 20 mL. H_2O was treated with 11 g. of crude Na salt of C,N-diformylglycine Et ester and neutralized with AcOH . After 15 h., NaHCO_3 was added and the dried CHCl_3 exts. (120 mL.) were concd. to give 6.55 g. of crude product, converted by treatment with 65.5 mL. of 10% HCl in EtOH to 4.4 g. of 2-(aminocarbethoxymethyl)-3-methylthiazolidine-2HCl (IX), m. $169-70^\circ$ (decompn.). IX (10.0 g.) in 36.1 mL. of 2N NaOH and 35 mL. EtOH was stirred with 6.6 g. $\text{PhCH}_2\text{CS}_2\text{Me}$ for 45 h., yielding 6.2 g. of colorless prisms of 2-[(phenylthioacetamido)carbethoxymethyl]-3-methylthiazolidine (X), m. $100-100.5^\circ$. Addn. of 5.0 g X in 20 mL. CHCl_3 to 8.6 g. PhSO_3Ag and 2.5 mL. pyridine in 70-mL. CHCl_3 gave no identifiable org. products. The action of PhSO_3Ag on Me α -phenylthioacetamido- β,β -diethoxypropionate yielded a product from which Me-benzylpenaldate and 2-benzyloxazole-4-carboxylic acid were isolated. By the PCl_5 method it has been possible to prep. 4-(2-thiazolyl)-2-benzyl-5-ethoxyoxazole and 2-(p-nitrophenyl)-4-(5,5-dimethyl-4-carbomethoxy-2-thiazolyl)-5-ethoxyoxazole. Attempts to introduce a CHO group into the 4-position of 2-phenyl-5-ethoxyoxazole (XI) using PhNMeCHO and POCl_3 gave 2-phenyl-4-anilinomethylene-5-oxazoline. With AcNHBr , XI gave 2-phenyl-4-bromo-5-ethoxyoxazole, b.p. 128° . The oxidn. of 2-phenyl-4-methyl-5-ethoxyoxazole with SeO_2 , CrO_3 or CrO_2Cl_2

resulted only in far-reaching breakdown. Condensation of $\text{PhCH}_2\text{CH}_2\text{COCO}_2\text{H}$ with AcNH_2 or AmCONH_2 gave α -acetamido- and α -caproyl-amino- γ -phenylisocrotonic acid (XII). Treatment of the Et ester of XII with PCl_5 afforded 2-amyl-4-styryl-5-ethoxyoxazole (XIII), disrupted by ozonization with prodn. of BzOH and $\text{H}_2\text{NCOCO}_2\text{Et}$. XIII (5.7 g.) in 100 mL. glacial AcOH was stirred with 9.0 g. of $\text{Pb}(\text{OAc})_4$ for 3 h., yielding 6.1 g. of 2-(1-acetoxymyl)-4-styryl-5-ethoxyoxazole, m. $90-1^\circ$, degraded by distn. with loss of AcOH to 2-(1-pentenyl)-4-styryl-5-ethoxyoxazole (XIV), m. 100° , reduced catalytically to XIII. Oxidn. of 2.83 g. XIV in 30 mL. tert-BuOH contg. 0.75 g. H_2O_2 and 30 mg. OsO_4 at $40-50^\circ$ for 2 h. produced PrCHO and 5-ethoxy-4-styryloxazole-2-carboxaldehyde, m. 130.5° , converted into the thiazolidine, m. 169° , using DL-penicillamine. Cyclization of $\text{AmCONHCH}(\text{CO}_2\text{Et})_2$ in dry alc. free CHCl_3 with PCl_5 , yielded 2-amyl-5-ethoxyoxazole-4-carboxylic acid (XIV), m. 63.4° , which on refluxing with PCl_5 in CHCl_3 gave Et 2-amyl-5-chlorooxazole-4-carboxylate (XV), b. 106° , catalytically reduced over Pd-BaSO_4 in xylene to 2-amyl-5-chlorooxazole-4-carboxylate, acidified to the free acid (XVa), m. $93-4^\circ$, converted by alc. EtONa to XIV. Treatment of 2 g. XVa with 1.09 g. PCl_5 in 10 mL. CHCl_3 and distn. produced the corresponding acid chloride, b. 96° , converted by $(\text{NH}_4)_2\text{CO}_3$ in aq. NH_4OH to the amide, m. 90° , which, distd. with **P205**, gave 2-amyl-5-chloro-4-cyanooxazole (XVb), b. 157° . Redn. of 3.0 g. XVb in a suspension of 5.7 g. anhyd. SnCl_2 in 40 mL. dry ether yielded unstable 2-amyl-5-chloro-oxazole-4-carboxaldehyde (XVI) (dinitrophenylhydrazone, m. $109-10^\circ$), rearranging in 3 days at room temp. or on low pressure distn. to 2-amyl-5-chlorooxazole-4-carboxylic acid chloride. Despite its instability, XVI readily combined with D-penicillamine-HCl to produce D-2-(2-amyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylic acid-HCl, m. $150-2^\circ$ (decompn.). A similar series of compds. starting with Et 2-phenyl-5-ethoxyoxazole-4-carboxylate (XVII) and proceeding to the thiazolidine was later prepd. XVII was saponified to the cryst. acid (XVIIa), m. 148° , converted to the acid chloride (XVIIb), m. $105-6^\circ$, and to Et 2-phenyl-5-chlorooxazole-4-carboxylate, m. 68° , by refluxing in xylene for 1 h. The corresponding acid (XVIII), m. $178-4^\circ$ (decompn.), was converted through the acid chloride, m. $118-20^\circ$, the amide, m. 183° , and the cyano compd., m. 112° , to 2-phenyl-5-chlorooxazole-4-carboxaldehyde (XIX), m. $91-3^\circ$. The addn. of 1.14 g. aldehyde in 5 mL. EtOH and 10 mL. Et_2O to 0.93 g. D-penicillamine-HCl in 5 mL. H_2O and 0.65 g. AcONa , and passage of HCl through a filtered ethereal soln. of the reaction product, yielded 1.5 g. of 2-(2-phenyl-5-chloro-4-oxazolyl)-5,5-di-methylthiazolidine-4-carboxylic acid-HCl, m. 178° (decompn.); Me ester-HCl, m. $120-2^\circ$; free acid, m.

166°; Me ester, m. 154°; PhCH₂ ester, m. 116-7°. The thiazolidine exhibited a low order of antibiotic activity. A similar series of 2-benzylloxazole derivs. have been prepd. but the corresponding thiazolidine was inactive: 2-benzyl-5-ethoxy-oxazole-4-carboxylic acid, m. 118° (decompn.); Et ester, b0.1 165°; acid chloride, m. 81-2°; 2-benzyl-5-chlorooxazole-4-carboxylic acid, m. 183° (decompn.); Et ester, b0.02 170-5°; acid chloride, m. 156-7°; cyano compd., m. 49-50°; aldehyde [dinitrophenylhydrazone, m. 173°; semicarbazone, m. 185° (decompn.)]; 2-(2-benzyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylic acid-HCl, m. 176-7° (decompn.). By refluxing 223 mg. XVIII in 3 mL. EtOH with 40 mg. Na, the Cl was replaced by the EtO group with formation of the corresponding acid, XVIIa. Distn. of the aldehyde XIX at 0.1 mm. gave 2-phenylloxazole-4-carboxylic acid chloride, m. 107-8°, transformed by stirring with cold concd. aq. NH₄OH to the amide. Similarly the acid chloride XVIIb was converted to the amide, m. 118-19°, rearranged by heating for a few min. at 140° to Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 183deg;. All oxazoles found to undergo rearrangement may be formulated as 5-substituted oxazoles having a CO group in the 4-position, the general case being $N:CR'.O.CR3:CCOR2 \rightarrow N:CR'.O.CR2:CCOR3$. Known examples of rearrangement are tabulated. Since the mol. is unstable when R₃ and R₂ are Et and Cl, resp., or when R₃ and R₂ are Cl and H, resp., it is deduced that the ethoxy aldehydes should show too great stability for successful synthesis. Cyclization of AmCONHCHCNCO₂Et with P2O₅ in CHCl₃ gave 2-amyl-4-cyano-5-ethoxyoxazole, b0.03 98°, not reduced to the aldehyde by SnCl₂ in Et₂O. No 4-acetyloxazole was obtained from the MeMgI reaction product but the isolation of Et α-caproylaminoacetoacetate (dinitrophenylhydrazone, m. 166-7°) indicated oxazole ring cleavage. The dehydration of 2-phenyl-5-ethoxyoxazole-4-carboxamide with POCl₃ or the ethylation with MeCHN₂ of the crude oxazolone obtained by treating BzNHCHCNCO₂H with Ac₂O produced 2-phenyl-4-cyano-5-ethoxyoxazole, m. 77°. The previously unknown 5-aminooxazoles were prepd. thus: treatment of 7 g. BzNHCH(CN)CO₂Et, m. 138°, in 125 mL. CHCl₃ with 6.2 g. PCl₅ gave 4.5 g. Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 185°, also prepd. by the action of POCl₃ on Bz-NHCH(CONH₂)CO₂Et. Condensation of 1.18 g. H₂NCH-(CO₂Et)₂ with 1.13 g. PhNH₂ by heating for 30 min. at 110° gave the alternative compd., formulated as 2-phenyl-4-carbethoxy-5-imidazolone, m. 275°. Similarly were prepd. Et 2-benzyl-5-aminooxazole-4-carboxylate (XX), m. 124° and the corresponding 2-benzyl-4-carbethoxy-5-imidazolone, m. 254° (decompn.); 2-(1-pentenyl)-4-carbethoxy-5-aminooxazole, m. 105°; 2-amyl-4-carbethoxy-5-aminooxazole (XXa), m.

104° and the corresponding 2-amyl-4-carbethoxy-5-imidazolone., m. 230° (decompn.). On heating at 170° for 5 min., XXa was entirely converted into AmCONHCH(CN.)CO₂Et, m. 83°. Heating either XX or PhCH₂CONHCH(CN)CO₂Et at 160-70° for 15 min. produced an equil. mixt. with the open chain ester predominating. This same mixt. was formed by heating 2-benzyl-5-ethoxyoxazole-5-carboxylic amide, probably through initial rearrangement to the aminooxazole. Stirring 35 g. NCCH₂CO₂CH₂Ph in 40 mL. of chilled glacial AcOH with satd. aq. NaNO₂ (16.5 g.) yielded 29 g. NCC(NOH)CO₂CH₂Ph, m. 119°, reduced with Al-Hg to NCC(NH₂)CO₂CH₂Ph, m. 95°, and benzoylated to NCCH(NHBz)CO₂CH₂Ph, m. 130°, converted by heating at 160° for 5 min. to 2-phenyl-4-carbobenzyloxy-5-aminooxazole, m. 203°. The 4-carbethoxy-5-aminooxazoles are feebly basic substances whose HCl salts dissociate readily. XXa.HCl, on boiling with ethereal EtOH gave AmCONHCH(CONH₂)CO₂Et, m. 150-1°, along with NH₄Cl. Treatment of 1 g. XXa in 10 mL. dry Et₂O at -15° with NOCl gave a low yield of Et 2-amyloxazole-4-carboxylate, m. 92-3°. Formylation of 15 g. BzNHCH₂CN in 200 mL. HCO₂Et and 100 mL. benzene by addn. of NaOEt (from 2.16 g. Na) in 100 mL. benzene produced, after treatment of the intermediate BzNHC(:CHONa)CO₂H with dil. H₂SO₄ to pH 4, 2-phenyl-5-aminooxazole-4-carboxaldehyde (XXI), m. 172-3°, probably in the tautomeric form. Formylation of AmCONHCH₂CN and distn. of the product yielded 2-amyloxazole-4-carboxylic acid amide, m. 154-5°, evidently by rearrangement of XXI. The action of POCl₃ on Bz-NHCH(CONH₂)₂ and AmCONHCH(CONH₂)₂, m. 231°, gave 2-phenyl-5-amino-4-cyanooxazole, m. 233° (Ac deriv., m. 202-3°), and 2-amyl-5-amino-4-cyanooxazole, m. 117°. These aminooxazoles could not be reduced to aldehydes.

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49:15976 Original Reference No. 49:3137a-i,3138a-i,3139a-i,3140a-i,3141a-i,3142a-i,3143a-i,3144a-i,3145a-i,3146a-i,3147a-i,3148a-i,3149a-i,3150a-i,3151a-b Oxazoles and oxazolones. Cornforth, J. W.; Clarke, H. T.; et al. (Oxford Univ.; Princeton Univ. Press). Chemistry of Penicillin 688-848 (Unavailable) 1949.
GI For diagram(s), see printed CA Issue.
AB OXAZOLE SECTION: New methods for constructing the oxazole ring have been devised and the behavior of functional groups elucidated. The synthesis of oxazoles and imidazoles from K β -hydroxy- α -(α -alkoxyalkylideneamino)acrylates is given. A mixt. of 51.1 g. AmCN and 24.5 g. EtOH was kept with 19.2 g. dry HCl below 0° for 2 wk, decompd. with 74 g. K₂CO₃ in Et₂O and distd. The crude AmC(OEt):NH (62.4 g.), b₁₁ 52-65°, was shaken with cold aq. H₂NCH₂CO₂Et.HCl for 1 h. The upper layer was fractionated to yield Et α -ethoxycaprylideneaminoacetate (I), b_{0.5} 91°, sapond. on gentle warming to AmCO₂Et. The corresponding Me α -methoxycaprylideneaminoacetate (Ia), b_{0.1} 74°, was similarly prepd. A soln. of 0.85 g. K in 2.5 g. EtOH and 14 g. Et₂O was dild. to 50 mL. with Et₂O, cooled to -15° and treated with a similarly cooled mixt. of 4.85 g. I and 3.2 g. HCO₂Et, yielding after 3 h. at -10°, 2.6 g. of hygroscopic needles of C₅H₁₁C(OEt):NC(CO₂Et):CHOK (II). The corresponding K Me

β -hydroxy- α -(α -methoxycaprylideneamino) acrylate (IIa) was obtained in 3.2 g.-yield from 3.75 g. Ia. Treatment of 2.6 g. II and 1.25 g. DL-penicillamine in 5 cc. EtOH with alc.-HCl gave cryst. DL-N-caproylpenicillamine, m. 137-8°. Treatment of II with ethereal HCl produced Et 2-amyloxazole-4-carboxylate, b0.07 99° (dinitrophenyl-hydrazone, m. 165-6°; amide, m. 152°) sapond. to 2-amyloxazole-4-carboxylic acid, m. 92-3° (PhNH₂ salt. m.98.5-9.5°) readily decarboxylated to 2-amyloxazole, b. 172-3°; picrate, m. 84.5-5.5°. This general synthesis of 2-substituted oxazoles and their 4-carboxylic acids has been extended to Et 2-phenyloxazole-4-carboxylate, m. 69-70°, the corresponding acid, m. 209°, and carried through to the known 2-phenyloxazole. The method can be also applied to the synthesis of imidazoles. Treatment of I with aq. NH₄OH gave 2-amylimidazole-4-carboxylic acid, m. 230° (decompn.); with MeNH₂.HCl or alc. H₂NCH₂CO₂Et.HCl, I produced, resp., Et 2-amyl-1-methylimidazole-4-carboxylate (III), m. 42-3°, and Et 2-amylimidazole-4-carboxylate-1-acetate (IIIa), m. 61°. Similarly, Ia gave Me 2-amyl-1-methylimidazole, m. 66.7°, and Me 2-amylimidazole-4-carboxylate-1-acetate, m. 107°. Hydrolysis of III and IIIa yielded 1-methyl-2-amylimidazole-4-carboxylic acid, m. 121-3°, and 2-amyl-4-carboxyimidazole-1-acetic acid, m. 132-4°. Starting from PhCH₂CN, Et 2-benzylimidazole-4-carboxylate-1-acetate, m. 111-2°, was likewise prepd., converted by treating with MeOH into a Me Et ester. On heating with aq. NH₄OH and with PhNH₂, 2-amyloxazole-4-carboxylic acid was converted into 2-amylimidazole, m. 33-4° and 1-phenyl-2-amylimidazole, m. 143-4°. Synthesis of oxazoles by rearrangement of oxazolones. The Na salt of 2-benzyl-4-hydroxymethylene-5-oxazolone (2.7 g.) in 50 mL. abs. MeOH was treated with 5 mL. abs. Et₂O contg. 0.38 g. HCl. The gummy product (2.28 g.) was taken up in 10 mL. abs. MeOH and heated for 30 min. with 6.2 mL. H₂O contg. 0.42 g. NaOH. The residue on evapn. was dissolved in 10 mL. of iced H₂O, acidified with dil. HCl to pH 6.5 and extd. with Et₂O, yielding 700 mg. 2-benzyloxazole-4-carboxylic acid, m. 158°. On heating at 220°, crude 2-phenyl-4-(α -hydroxyethylidene)-5-oxazolone rearranged to 2-phenyl-5-methyloxazole (IV), m. 184-5° (decompn.). Similarly, on heating to 230°, Na 4-hydroxymethylene-g-amyl-5-oxazolone rearranged to 2-amyloxazole-4-carboxylic acid. Evapn. of 2-(1-pentenyl)-4-(hydroxymethylene)-5-oxazolone in NaOH and fusion of the residue at 250° under reduced pressure yielded 2-pentenyl-oxazole-4-carboxylic acid, m. 145-7°. Incidental syntheses of oxazole derivs. The action of PhSO₃Ag on Me thiobenzylpenaldate di-Et acetal produced colorless prisms of 2-benzyloxazole-4-carboxylic acid, m. 156-7° and the dehydration of Et α -benzylamino-acetoacetate gave Et

2-phenyl-5-methyloxazole-4-carboxylate, m. 51-2°, hydrolyzed to the acid, m. 180-1°, decarboxylated at 220° in the presence of a trace of CuO to IV. Thus a reaction known to succeed with α -acylamino ketones and carboxylic esters is extended to β -keto esters. The 2-substituted oxazoles and their 4-carboxylic acids and esters are feebly basic, readily oxidized by cold aq. KMnO₄ but stable to Br in CCl₄. The ring opens on warming with 2,4-(O₂N)₂-C₆H₃NHNH₂ in 2N HCl with a tendency to formation of glyoxal osazone derivs. Rosenmund redn. of 2-amyloxazole-4-carboxylic acid chloride produced 2-amyloxazole-4-carboxaldehyde, b₈ 108° (2,4-dinitrophenylhydrazide, m. 172-3°), converted by warming with D-penicillamine-HCl in AcOH to the thiazolidine, devoid of antibiotic properties. From the corresponding Et ester, 2-benzyl-4-carboxyoxazole hydrazide, m. 81-3° and benzylamide, m. 121-2° were prepd. In attempts to synthesize the thiazolidine-oxazolone structure for penicillin, attention was directed to the prepn. of 5-alkoxyoxazoles and many variations of the general method of dehydrating α -acylamino esters with **P205** were introduced. By the use of PCl₅, **P205**, POCl₃, SOCl₂, and PhSO₂Cl, the following new oxazoles were prepd. (substituent given): 2-Ph, 5-MeO, b₉ 141°; 2-Ph, 5-PhCH₂O, m. 56°; 2-PhCH₂, 5-EtO, b₁₅ 152-4°; 2-PhCH₂, 5-MeO, m. 31-2°; 2-Am, 5-EtO, b_{0.8} 82-5°; 2-Am, 5-MeO, b_{1.0} 60-65°; 2-(1-C₅H₉), 5-EtO, b₂₀ 125-8° (C₅H₉ = pentenyl); 2-(1-C₅H₉), 5-MeO, b₁₅ 108-10°; 2-PhCH:CH, 5-EtO, m. 35°; 2-PhCH:CH, 5-PhCH₂O, picrate, m. 135° (decompn.); 2-Ph, 4-Me, 5-EtO, b₁₀ 151°; 2-Ph, 4-Me, 5-PhCH₂O, picrate, m. 112-13°; 2-PhCH₂, 4-Me, 5-EtO, b₁₅ 145-50°; 2-Am, 4-Me, 5-EtO, b₃ 92°; 2,4-Ph₂, 5-EtO, m. 47-8°; 2-Ph, 4-PhCH₂, 5-EtO, picrate, m. 105°; 2-Ph, 4-PhCH₂, 5-PhCH₂O, picrate, m. 117°; 2,4-(PhCH₂)₂, 5-EtO, b_{0.3} 145-50°; 2-Am, 4-PhCH:CH, 5-EtO, m. 92°; 2-Ph, 4-CO₂Et, 5-EtO, m. 75°; 2-Am, 4-CO₂Et, 5-EtO, b_{0.1} 122-5°; 2-(1-C₅H₉), 4-CO₂Et, 5-EtO, b_{0.2} 125°; 2-PhCH₂, 4-CO₂Et, 5-EtO, b_{0.1} 165°. The possibility of converting an alkoxyoxazole to the corresponding oxazolone was realized by the catalytic hydrogenation of 2 g. of 2-phenyl-5-benzyloxyoxazole in 30 mL. dry dioxane in the presence of Pd-black to 2-phenyl-5-oxazolone, m. 91°. The converse reaction, transformation of an oxazolone to an alkoxyoxazole, has also been achieved. Methylation of 3 g. of 2-phenyl-4-carbethoxy-5-oxazolone with 500 mg. CH₂N₂ in 50 mL. Et₂O yielded 2-phenyl-4-carbethoxy-5-methoxyoxazole, m. 72°. Similarly, methylation of 2-phenyl-4-carbomethoxy-2-oxazolin-5-one gave 2-phenyl-4-carbomethoxy-5-methoxyoxazole, m. 98°, identical with that prepd. by the dehydration of BzNHCH(CO₂Me)₂ with PCl₅ in CCl₄. Attempts to obtain 5-alkoxyoxazole-4-carboxaldehydes covered a wide range. Formylation of BzNHCH₂CO₂Et and condensation

with PhCH_2NH_2 in Et_2O gave Et β -benzylamino- α -benzamidoacrylate, $\text{R}'\text{NHCH}:\text{C}(\text{CO}_2\text{Et})\text{NHCOR}$ (V; $\text{R} = \text{Ph}$, $\text{R}' = \text{PhCH}_2$), m. 108° , cyclized by PBr_3 , POCl_3 or PCl_5 to 2-phenyl-4-benzylaminomethylene-5-oxazolone (VI), m. $134-7$; Ac deriv., m. 140° . In the same way, Et β -benzylamino- α -phenylacetamido acrylate (VIa) with PBr_3 gave 2-benzyl-4-benzylaminomethylene-5-oxazolone (VIb). Dehydration of Et α -benzamido- β,β -diethoxypropionate with PCl_5 - POCl_3 yielded 2-phenyl-4-(ethoxymethylene)5-oxazolone (VII). Distn. of benzyl α -benzamido- β,β -diethoxypropionate gave a mixt. of products including benzyl α -benzamido- β -ethoxyacrylate, m. $108-10^\circ$; benzyl 2-phenyloxazole-4-carboxylate, m. $106-7^\circ$; and VII. Attempts were made to cyclize α -benzyl- β -methyl-DL-phenylpenicilloate, $\text{HN}.\text{CH}(\text{CO}_2\text{R}')\text{.CMe}_2.\text{S}.\text{CHCH}(\text{NHCOR})\text{CO}_2\text{CH}_2\text{Ph}$ (VIII, $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$) (VIIIa), m. 130° ; dibenzyl-DL-phenylpenicilloate (VIII, $\text{R} = \text{Ph}$, $\text{R}' = \text{PhCH}_2$) (VIIIb), m. $107-8^\circ$; and DL-2-(carboxy-1-hexenoylaminoethyl)-5,5-dimethyl-4-carbomethoxythiazolidine benzyl ester (VIII, $\text{R} = 1\text{-pentenyl}$, $\text{R}' = \text{Me}$) (VIIIc). The action of PCl_5 on VIII and VIIIa gave definite evidence of formation of thiazolidinylalkoxyoxazoles and cyclization of VIIIb and chromatog. purifn. of the product gave benzyl 2-(2-phenyl-5-benzyloxy-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylate, m. $120-5^\circ$, absorption band at 2850 A . This reduced in EtOAc using a Pd-BaSO_4 catalyst with 2 mol H, corresponding to removal of 2 PhCH_2 groups, yielded a product with no-antibiotic activity. The simpler thiazolidines were also investigated. The reaction of 3-methyl-2-(benzamidocarbethoxymethyl)-thiazolidine with PCl_5 gave a Cl-contg. product, converted by NaHCO_3 to a probable sulfoxide. With PCl_3 , a product was obtained, which was converted by aq. KOH to 2-phenyl-4-hydroxymethylene-5-oxazolone. β -Methylaminoethyl mercaptan-HI (from 15 g. of 2-methylthiazoline-MeI) in 20 mL. H_2O was treated with 11 g. of crude Na salt of C,N-diformylglycine Et ester and neutralized with AcOH . After 15 h., NaHCO_3 was added and the dried CHCl_3 exts. (120 mL.) were concd. to give 6.55 g. of crude product, converted by treatment with 65.5 mL. of 10% HCl in EtOH to 4.4 g. of 2-(aminocarbethoxymethyl)-3-methylthiazolidine-2HCl (IX), m. $169-70^\circ$ (decompn.). IX (10.0 g.) in 36.1 mL. of 2N NaOH and 35 mL. EtOH was stirred with 6.6 g. $\text{PhCH}_2\text{CS}_2\text{Me}$ for 45 h., yielding 6.2 g. of colorless prisms of 2-[(phenylthioacetamido)carbethoxymethyl]-3-methylthiazolidine (X), m. $100-100.5^\circ$. Addn. of 5.0 g X in 20 mL. CHCl_3 to 8.6 g. PhSO_3Ag and 2.5 mL. pyridine in 70-mL. CHCl_3 gave no identifiable org. products. The action of PhSO_3Ag on Me α -phenylthioacetamido- β,β -diethoxypropionate yielded a product from which Me-benzylpenaldate and 2-benzyloxazole-4-carboxylic acid were isolated. By the PCl_5 method it has been possible to prep. 4-(2-thiazolyl)-2-benzyl-5-ethoxyoxazole and

2-(p-nitrophenyl)-4-(5,5-dimethyl-4-carbomethoxy-2-thiazolinyl)-5-ethoxyoxazole. Attempts to introduce a CHO group into the 4-position of 2-phenyl-5-ethoxyoxazole (XI) using PhNMeCHO and POCl₃ gave 2-phenyl-4-anilinomethylene-5-oxazoline. With AcNHBr, XI gave 2-phenyl-4-bromo-5-ethoxyoxazole, b_{0.8} 128°. The oxidn. of 2-phenyl-4-methyl-5-ethoxyoxazole with SeO₂, CrO₃ or CrO₂Cl₂ resulted only in far-reaching breakdown. Condensation of PhCH₂CH₂COCO₂H with AcNH₂ or AmCONH₂ gave α-acetamido- and α-caproyl-amino-γ-phenylisocrotonic acid (XII). Treatment of the Et ester of XII with PCl₅ afforded 2-amyl-4-styryl-5-ethoxyoxazole (XIII), disrupted by ozonization with prodn. of BzOH and H₂NCOCO₂Et. XIII (5.7 g.) in 100 mL. glacial AcOH was **stirred** with 9.0 g. of Pb(OAc)₄ for 3 h., yielding 6.1 g. of 2-(1-acetoxyamyl)-4-styryl-5-ethoxyoxazole, m. 90-1°, degraded by distn. with loss of AcOH to 2-(1-pentenyl)-4-styryl-5-ethoxyoxazole (XIV), m. 100°, reduced catalytically to XIII. Oxidn. of 2.83 g. XIV in 30 mL. tert-BuOH contg. 0.75 g. H₂O₂ and 30 mg. OsO₄ at 40-50° for 2 h. produced PrCHO and 5-ethoxy-4-styryloxazole-2-carboxaldehyde, m. 130.5°, converted into the thiazolidine, m. 169°, using DL-penicillamine. Cyclization of AmCONHCH(CO₂Et)₂ in dry alc. free CHCl₃ with PCl₅, yielded 2-amyl-5-ethoxyoxazole-4-carboxylic acid (XIV), m. 63.4°, which on refluxing with PCl₅ in CHCl₃ gave Et 2-amyl-5-chlorooxazole-4-carboxylate (XV), b_{0.3} 106°, catalytically reduced over Pd-BaSO₄ in xylene to 2-amylloxazole-4-carboxylate, acidified to the free acid (XVa), m. 93-4°, converted by alc. EtONa to XIV. Treatment of 2 g. XVa with 1.09 g. PCl₅ in 10 mL. CHCl₃ and distn. produced the corresponding acid chloride, b_{0.3} 96°, converted by (NH₄)₂CO₃ in aq. NH₄OH to the amide, m. 90°, which, distd. with P₂O₅, gave 2-amyl-5-chloro-4-cyanooxazole (XVb), b_{0.15} 72°. Redn. of 3.0 g. XVb in a suspension of 5.7 g. anhyd. SnCl₂ in 40 mL. dry ether yielded unstable 2-amyl-5-chloro-oxazole-4-carboxaldehyde (XVI) (dinitrophenylhydrazone, m. 109-10°), rearranging in 3 days at room temp. or on low pressure distn. to 2-amylloxazole-4-carboxylic acid chloride. Despite its instability, XVI readily combined with D-penicillamine-HCl to produce D-2-(2-amyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylic acid-HCl, m. 150-2° (decompn.). A similar series of compds. starting with Et 2-phenyl-5-ethoxyoxazole-4-carboxylate (XVII) and proceeding to the thiazolidine was later prepd. XVII was sapond. to the cryst. acid (XVIIa), m. 148°, converted to the acid chloride (XVIIb), m. 105-6°, and to Et 2-phenyl-5-chlorooxazole-4-carboxylate, m. 68°, by refluxing in xylene for 1 h. The corresponding acid (XVIII), m. 178-4° (decompn.), was converted through the acid chloride, m. 118-20°, the amide, m. 183°, and the cyano compd., m. 112°, to 2-phenyl-5-chlorooxazole-4-carboxaldehyde (XIX), m.

91-3°. The addn. of 1.14 g. aldehyde in 5 mL. EtOH and 10 mL. Et2O to 0.93 g. D-penicillamine-HCl in 5 mL. H2O and 0.65 g. AcONa, and passage of HCl through a filtered ethereal soln. of the reaction product, yielded 1.5 g. of 2-(2-phenyl-5-chloro-4-oxazolyl)-5,5-di-methylthiazolidine-4-carboxylic acid-HCl, m. 178° (decompn.); Me ester-HCl, m. 120-2°; free acid, m. 166°; Me ester, m. 154°; PhCH2 ester, m. 116-7°. The thiazolidine exhibited a low order of antibiotic activity. A similar series of 2-benzyloxazole derivs. have been prepd. but the corresponding thiazolidine was inactive: 2-benzyl-5-ethoxy-oxazole-4-carboxylic acid, m. 118° (decompn.); Et ester, b0.1 165°; acid chloride, m. 81-2°; 2-benzyl-5-chlorooxazole-4-carboxylic acid, m. 183° (decompn.); Et ester, b0.02 170-5°; acid chloride, m. 156-7°; cyano compd., m. 49-50°; aldehyde [dinitrophenylhydrazone, m. 173°; semicarbazone, m. 185° (decompn.)]; 2-(2-benzyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylic acid-HCl, m. 176-7° (decompn.). By refluxing 223 mg. XVIII in 3 mL. EtOH with 40 mg. Na, the Cl was replaced by the EtO group with formation of the corresponding acid, XVIIa. Distn. of the aldehyde XIX at 0.1 mm. gave 2-phenyloxazole-4-carboxylic acid chloride, m. 107-8°, transformed by stirring with cold concd. aq. NH4OH to the amide. Similarly the acid chloride XVIIb was converted to the amide, m. 118-19°, rearranged by heating for a few min. at 140° to Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 183deg;. All oxazoles found to undergo rearrangement may be formulated as 5-substituted oxazoles having a CO group in the 4-position, the general case being $N:CR'.O.CR3:CCOR2 \rightarrow N:CR'.O.CR2:CCOR3$. Known examples of rearrangement are tabulated. Since the mol. is unstable when R3 and R2 are Et and Cl, resp., or when R3 and R2 are Cl and H, resp., it is deduced that the ethoxy aldehydes should show too great stability for successful synthesis. Cyclization of AmCONHCHCNCOC2Et with **P205** in CHCl3 gave 2-amyl-4-cyano-5-ethoxyoxazole, b0.03 98°, not reduced to the aldehyde by SnCl2 in Et2O. No 4-acetyloxazole was obtained from the MeMgI reaction product but the isolation of Et α -caproylaminoacetoacetate (dinitrophenylhydrazone, m. 166-7°) indicated oxazole ring cleavage. The dehydration of 2-phenyl-5-ethoxyoxazole-4-carboxamide with POCl3 or the ethylation with MeCHN2 of the crude oxazolone obtained by treating BzNHCHCNCOC2H with Ac2O produced 2-phenyl-4-cyano-5-ethoxyoxazole, m. 77°. The previously unknown 5-aminooxazoles were prepd. thus: treatment of 7 g. BzNHCH(CN)CO2Et, m. 138°, in 125 mL. CHCl3 with 6.2 g. PCl5 gave 4.5 g. Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 185°, also prepd. by the action of POCl3 on Bz-NHCH(CONH2)CO2Et. Condensation of 1.18 g. H2NCH-(CO2Et)2 with 1.13 g. PhNHOEt by heating for 30 min. at 110° gave the

alternative compd., formulated as 2-phenyl-4-carbethoxy-5-imidazolone, m. 275°. Similarly were prepd. Et 2-benzyl-5-aminooxazole-4-carboxylate (XX), m. 124° and the corresponding 2-benzyl-4-carbethoxy-5-imidazolone, m. 254° (decompn.); 2-(1-pentenyl)-4-carbethoxy-5-aminooxazole, m. 105°; 2-amyl-4-carbethoxy-5-aminooxazole (XXa), m. 104° and the corresponding 2-amyl-4-carbethoxy-5-imidazolone, m. 230° (decompn.). On heating at 170° for 5 min., XXa was entirely converted into AmCONHCH(CN)CO₂Et, m. 83°. Heating either XX or PhCH₂CONHCH(CN)CO₂Et at 160-70° for 15 min. produced an equil. mixt. with the open chain ester predominating. This same mixt. was formed by heating 2-benzyl-5-ethoxyoxazole-5-carboxylic amide, probably through initial rearrangement to the aminooxazole. Stirring 35 g. NCCH₂CO₂CH₂Ph in 40 mL. of chilled glacial AcOH with satd. aq. NaNO₂ (16.5 g.) yielded 29 g. NCC(NOH)CO₂CH₂Ph, m. 119°, reduced with Al-Hg to NCC(NH₂)CO₂CH₂Ph, m. 95°, and benzoylated to NCCH(NHBz)CO₂CH₂Ph, m. 130°, converted by heating at 160° for 5 min. to 2-phenyl-4-carbobenzyloxy-5-aminooxazole, m. 203°. The 4-carbethoxy-5-aminooxazoles are feebly basic substances whose HCl salts dissoc. readily. XXa.HCl, on boiling with ethereal EtOH gave AmCONHCH(CONH₂)CO₂Et, m. 150-1°, along with NH₄Cl. Treatment of 1 g. XXa in 10 mL. dry Et₂O at -15° with NOCl gave a low yield of Et 2-amylloxazole-4-carboxylate, m. 92-3°. Formylation of 15 g. BzNHCH₂CN in 200 mL. HCO₂Et and 100 mL. benzene by addn. of NaOEt (from 2.16 g. Na) in 100 mL. benzene produced, after treatment of the intermediate BzNHC(:CHONa)CO₂H with dil. H₂SO₄ to pH 4, 2-phenyl-5-aminooxazole-4-carboxaldehyde (XXI), m. 172-3°, probably in the tautomeric form. Formylation of AmCONHCH₂CN and distn. of the product yielded 2-amylloxazole-4-carboxylic acid amide, m. 154-5°, evidently by rearrangement of XXI. The action of POCl₃ on Bz-NHCH(CONH₂)₂ and AmCONHCH(CONH₂)₂, m. 231°, gave 2-phenyl-5-amino-4-cyanooxazole, m. 233° (Ac deriv., m. 202-3°), and 2-amyl-5-amino-4-cyanooxazole, m. 117°. These aminooxazoles could not be reduced to aldehydes.

Satn. of 0.52 g. PhCH₂CSNHCH(CN)CO₂Et, m. 157°, treated in 5 mL. dry EtOH with dry HCl at -10° and the soln. evapd. after 12 h. at 20° in vacuo yielded 0.5 g. 2-benzyl-4-carbethoxy-5-aminothiazole, m. 180°. OXAZOLONE SECTION. Part. I.

General Chem. of Oxazolones. Prepn. of 2-Oxazolin-5-ones. The reaction of Ac₂O with α-acylamino acids is the most general procedure by which new oxazolones, O.CR:N.CR₁R₂.CO, have been prepd. (substituents given): 2-Me, 4-iso-Pr, b10 60°; 2-PhCH₂, 4-Me, b0.5-1.0 122-3°; 2-PhCH₂, 4-iso-Pr, b0.5 115-17°; 2,4-(PhCH₂)₂, oil; 2-Am, 4-PhCH₂, b5 135-8°; 2-(2-pentenyl), 4-PhCH₂, b1.0 155-7°; 2-PhCH₂, 4,4-Me₂ (I), m. 59.5°; 2-Ph, 4-iso-Bu, m. 56-7°; 2-PhCH₂, 4-sec-Bu, b2.0

137-9°; 2-Ph, 4,4-C₅H₁₀, m. 71°; 2-PhCH₂, 4-Me, 4-PhCH:CH, m. 56-7°; 2-Ph, 4-CO₂Et, m. 147-8°; 2-Am, 4-CO₂Et, oil; 2-Ph, 4-(p-MeOC₆H₄CH₂); 2-PhCH₂, 4-(p-MeOC₆H₄CH₂); and 2-PhCH₂, 4-iso-Bu. Similarly, heating 100 g. BzNHCH₂CO₂H (II) in 300 mL. Ac₂O at 100° yielded 49 g. 2-phenyl-2-oxazolin-5-one (III), m. 94-5°, the only monosubstituted oxazolone prep'd. by this method. By warming BzNHCHPhCH₂CO₂H in CHCl₃ with 1 equiv. of 2-benzyl-4-methyl-5-oxazolone, a good yield of 2-phenyl-4-benzyl-5-oxazolone, m. 68-9°, was obtained. Addn. of 1 g. NaNO₂ in 20 mL. H₂O to 3 g. of BzNHC(CONHNH₂):-CHPh in 30 mL. N HCl gave α-benzamidocinnamic azide, m. 113-4° (decompn.), converted on boiling with EtOH or treatment with pyridine at room temp. to 2-phenyl-4-benzylidene-5-oxazolone (IV). Similarly, Me₂C:C(NHBz)-CON₃ was converted to 2-phenyl-4-isopropylidene-5-oxazolone (IVa). These type II (unsatd. substituent at the 4-position) unsatd. oxazolines are formed more readily than the above-listed type I (satd. substituent at the 4-position) satd. oxazolones to which the azide conversion could not be extended. Redn. of IV over Pd-C gave 2-phenyl-4-benzyl-5-oxazolone (V), m. 67-8°. IVa was similarly reduced in dioxane to give an oil which, treated with PhNH₂ in benzene, produced Me₂CHCH(NHBz)CONHPh, m. 211-2°. The possibility arose that any reagent capable of transforming an acid to its chloride might be expected to convert an α-acylamino acid to the corresponding oxazolone. Thus treatment of II in 15 mL. dioxane with 2 mL. PBr₃ gave III. Similarly, 14.5 g. PhCH₂CONHCHMe₂CO₂H in 150 mL. dioxane was treated with 18 g. PBr₃. The solid product suspended in dioxane and treated with slight excess of CH₂N₂ in ether yielded I, converted by PhCH₂NH₂ into PhCH₂CONHCHMe₂CONH₂, m. 122-3°. Treatment of PhCH₂CHNHBzCO₂H in pyridine with PBr₃ likewise gave the known V. Attempts to prep. 2-benzyl-5-oxazolone from PhCH₂CONHCH₂CO₂H gave an unstable oil, converted by PhCH₂NH₂ into PhCH₂CONHCH₂CONHCH₂Ph. Conversion of PhCH:C(NHBz)CO₂H into IV was effected by POCl₃, SOCl₂, pyridine, by ClCH₂COCl and K₂CO₃, and by AcCl in dioxane. Oxazolones have been produced by treating PhCH₂OCOC₂H with acylamino acids. Apart from direct dehydration, three methods are known for the prepn. of type II oxazolones; the Erlenmeyer aldehydeacylglycine synthesis, the Bergmann-Stein reaction of N-(α-haloacyl)amino acids with Ac₂O, and the dehydration of β-hydroxy-α-acylamino acids. In that III reacts with Me₂CO in the presence of NaOAc to yield IVa in the absence of Ac₂O, it is suggested that III is an intermediate in the Erlenmeyer synthesis. In the presence of a little pyridine, BzH condenses with III to produce IV. Similarly, 2-phenyl-4-propylidene-5-oxazolone, m. 88-9°, was obtained in good yield from III and EtCHO. By adding Ac₂O dropwise with stirring to 17.9 g. II and 6.1 g. fused NaOAc in 580 mL. Me₂CO, refluxing for 3-4 h. at 59-62°, pouring the reaction mixt. over 200 g. ice and dilg. to 1500 mL. produced high yields (73%) of

relatively pure 2-phenyl-4-isopropylidene-5-oxazolone, m. 98°. Condensation of II with (EtO)₂CHCHO and Ac₂O gave 4,4'-glyoxalidenebis(2-phenyl-5-oxazolone), m. 325° (decompn.). Though no acyl interchange in the Erlmeyer synthesis occurs with II, the formation of 2-methyl-4-benzylidene-5-oxazolone occurs when either PhCH₂CONHCH₂CO₂H or AmCONHCH₂CO₂H (VI) is refluxed with BzH in the presence of Ac₂O and NaOAc. Refluxing VI (15.1 g.) with 13.1 g. AmCO₂Na and 61 g. (AmCO)₂O in 49 mL. Me₂CO for 24 h. at 75° gave α-caproyl-amino-β,β-dimethylacrylic acid, m. 162-3°, converted by melting and heating in vacuo at 180-90° into 2-amyl-4-isopropylidene-5-oxazolone, b0.03 60-2°. By Bergmann's method, 2-methyl-4-isopropylidene-5-oxazolone (VII) and 2-methyl-4-sec-butylidene-5-oxazolone were prepd. from Me₂CHCH₂CH(NHCOCH₂Cl)CO₂H and EtMeCHCH(NHCOCH₂Cl)CO₂H. Carter's method was used to prep. VII by the action of Ac₂O on Me₂C(OMe)CHNH₂CO₂H. Ring opening Reactions of Oxazolones. The general reaction of oxazolones with H₂O, ROH, RSH, NH₃, RNH₂ and RR'NH represented by O.CR:N.CR₁R₂.CO + HX → OCRHNCR₁R₂COX, suggested originally the thiazolidine-oxazolone formulation of penicillin. Comparison of the reactivity of V with that of IV showed the former to be rapidly hydrolyzed by 2N aq. acid or alkali under conditions not affecting the latter. V reacts with ROH more rapidly than III. In the presence of NaOMe or PhCH₂NMe₃-OH, IVa was converted quant. to Me₂C:C(BzNH)CO₂Me, m. 130-1°. The methanolysis of 2-benzyl-4-p-methoxybenzyl-5-oxazolone in dry abs. MeOH yielded (N-phenylacetyl-p-methoxyphenylalanyl)-p-methoxyphenylalanine, m. 199-200°. The formation of the dipeptide may be due to an "ortho-ester" reaction with the imino-ether form of the oxazolone. Reaction of PhCH₂SH with III and I yielded benzyl hippurate, m. 101-2° and Me₂CHCH(NHCOCH₂Ph)COSCH₂Ph, m. 138.5°. Almost all types of oxazolones react with PhCH₂NH₂ to form α-acylaminoacyl-benzylamides. The reaction of V with d-MePhCHNH₂ in dry dioxane was followed polarimetrically and at const. rotation, produced N-benzoylphenylalanine-d-N-α-phenylethylamide, m. 178-80°, [α]_{D23} 28.5° (c 1, dioxane). The strongly enolyzed 2-phenyl-4-carbethoxy-5-oxazolone formed a salt with PhCH₂NH₂, converted on heating in xylene to the benzylamide, m. 132°. The reaction of PhNH₂.HCl with III and 2-benzyl-4-sec-butyl-5-oxazolone gave the normal anilide and the corresponding acid. Reaction of V and 2-phenyl-4-isobutyl-5-oxazolone with L-HSCH₂CH(NH₂)CO₂Me produced the normal amides, m. 128-9°, and 131-5°, resp., the NH₂ group taking precedence over the SH group in the condensation. The action of N₂H₄ on oxazolones has been clarified. The addn. of 18 g.-phenyl-4-methyl-5-oxazolone to excess 60% N₂H₄.H₂O in EtOH and heating to 50-60° for 30 min. gave 17.5 g. benzoylalanine

hydrazide, m. 142-4°; benzylidene deriv., m. 193-4°. Treatment of IV with N₂H₄.H₂O also gave the normal hydrazide, PhCH:C(NHBz)CONHNH₂, m. 113-14°, converted by heating the corresponding azide in xylene to 2-oxo-4-benzylidene-6-phenyl-1,3,5-oxadiazine, m. 174° (decompn.). Conversion of Me₂C:C(NHBz)CON₃ similarly produced 2-oxo-4-isopropylidene-6-phenyl-1,3,5-oxadiazine, m. 166-8°. A mixt. of 5 g. IV, 10 mL. N₂H₄.H₂O and 3 mL. EtOH was refluxed for 30 min. yielding 4-benzamido-3-phenyl-5-pyrazolidone, m. 228-9°, identical with the product formed by refluxing PhCH:C(NHBz)CONHNH₂ (VIII), m. 157-8°, which N₂H₄.H₂O for 30 min. Similarly, the hydrazide Me₂C:C(NHBz)CONHNH₂, m. 192-4°, was converted into 3,3-dimethyl-4-benzoylamino-5-pyrazolidine, m. 106-8°. The hydrazide VIII was boiled in N NaOH and the sparingly sol. salt on acidification gave 6-hydroxy-5-benzyl-3-phenyl-1,2,4-triazine, m. 175-6°; Ac deriv., 187-8°. Oxidn. of XIII with K₃Fe(CN)₆ produced N,N'-bis(α-benzoylamino-5-pyrazolidine)hydrazine, m. 265°, together with a substance, m. 186-7°, with the probable structure PhCH:C.CH(OH).NBz.C-(CHPh).CH(OH).NBz, forming PhCH₂CH(NHBz)-(CO₂H) on alk. hydrolysis. REACTIONS OF TYPE II OXAZOLONES: Some reactions involving the double bond in type II oxazolones have been discovered. Treatment of IV in dry dioxane with 2 mol CH₂N₂ in dry Et₂O at 0° and allowing the soln. to stand overnight at room temp. gave product, C₁₇H₁₃O₂N, m. 142-3°. Addn. of liq. NH₃ to IVa with shaking and cooling in solid CO₂ gave a small yield of basic product, C₁₂H₁₇O₂N₃, m. 162-6°, probably by addn. of 2 mol NH₃. Addn. of H₂S and RSH to the double bond has been studied in connection with various syntheses of penicillamine. The addn., of 136 g. IVa in 675 mL. dry benzene to 3.38 g. Na in 675 mL. of chilled dry MeOH and 76.5 mL. PhCH₂SH produced Me₂CC(NHBz)CO₂Me, m. 137-8°, and Me₂C(SCH₂Ph)CH(NHBz)CO₂Me, m. 66-7°. The addn. probably takes place after ring opening, since the oxazolone can be replaced by an acrylic ester. Similarly, IV under like conditions, gave PhCH(SCH₂Ph)CH(NHBz)CO₂Me, m. 164°. There is no evidence of direct addn. of PhCH₂SH to the double bond. Addn. of H₂S to IVa and VII in the presence of Et₃N yielded Me₂C(SH)CH(NHBz)COSH and Me₂C(SH)CH(NHAc)COSH, resp. The initial step is probably the addn. of H₂S to the double bond. Anhyd. MeOH satd. with H₂S at 0° treated with IVa gave 2,5,5-trimethyl-2-thiazoline-4-carboxylic acid, b₂₅ 120°; picrate, m. 159°, probably formed by addn., followed by displacement. IV similarly yielded 2-phenyl-5,5-dimethyl-2-thiazoline-4-carboxylic acid, m. 124-6°. IVa was apparently converted by treatment with alc. NaSH to 2-phenyl-4-isopropylidene-5-thiazolone, m. 100.5-101.5°. The reactivity of the Me groups in IVa is sufficient to permit condensation reactions with BzH to produce 2-phenyl-4-benzylideneisopropylidene-5-oxazolone, m. 135°. A

mixt. of stereoisomers, m. 134-6°, was produced by heating a mixt. of 35.8 g. BzNHCH₂CO₂H, 32 g. PhCH:CHAc, 15 g. of fused NaOAc and 50 mL. Ac₂O for 3 h. at 100°. IVa is a pseudo-acid and exhibits weak violet fluorescence in Et₃N. On addn. of NaOMe to IVa in MeOH, the initial intense blue-violet fluorescence in UV light due to the presence of the propenyloxazole soon disappears with the formation of Me₂C:C(NHBz)CO₂Me by ring opening. Misc. REACTIONS OF OXAZOLONES. Excess PhMgBr was added to 6.0 g. 2-phenyl-4-methyl-5-oxazolone in Et₂O and after refluxing for 6 h. the reaction product was hydrolyzed and extd. with Et₂O, yielding 4.6 g. 1,1-diphenyl-2-benzoylamino-propanol, m. 192-3°. With AgClO₄ in benzene, III in EtOH gave a complex, m. 146° (decompn.). A similar cryst. compd., m. 172° (decompn.) was formed with 2-benzyl-4-methyl-5-oxazolone (IX). Formylation of 2,4-diphenyl-5-oxazolone apparently produced a stabilized enolic form, PhC:N.CPh:COH.O, m. 110°. Oxidn. of 2-phenyl-4-isobutyl- and 2-phenyl-4-benzyl-5-oxazolones with Hg(OAc)₂ gave the corresponding 4,4'-bisoxazolones, m. 138-42°, and 201-202.5°, resp. PSEUDO-OXAZOLONES. According to the method of Bergmann, 12 g. PhCHBrCONHCH₂CO₂H was added to 5 mL. dry pyridine and 100 mL. Ac₂O and after 2.5 h. at 0° was poured over ice. The solid product was dried over NaOH and crystd. from warm MeOH by cooling to -50°, yielding 64% of 2-benzylidenepseudooxazolone (2-benzylidene-3-oxazolin-5-one), m. 92-4°, hydrolyzed by 0.5N HCl in acetone to PhCH₂-CONH₂, m. 153-7°. An attempt to prep. 2-benzyl-4-methylene-5-oxazolone by Bergmann's method from Ph-CHClCONHCHMeCO₂H gave the potent skin irritant 2-benzylidene-4-methylpseudo-5-oxazolone (X), m. 105-115°, hydrolyzed by aq. acetone to PhCH₂CONH₂ and AcCO₂H, suggesting that the pseudooxazolones are intermediates in the Bergmann synthesis of type II oxazolones and that, in general, the latter are in dynamic equil. with the pseudooxazolones. In an attempt to use pseudooxazolones for the thiazolidine-oxazolone structure suggested for penicillin, Br was added to V and the product condensed with penicillamine (XI) in the presence of AcOK and AcOH. The low order of activity noted was probably due to BrCH₂COCO₂H which has an activity of 6 units per mg. against Gram-pos. organisms. X (1 g.) in 40 mL. pure AcOEt was hydrogenated at several atm. pressure in the presence of 2 g. active Raney Ni to IX, suggesting that the thiazolidine-oxazolone structure might be accessible by redn. of the corresponding pseudooxazolone. Ice-cold pyridine (20 mL.) in 65 mL. Me₂CO was mixed with 1 g. (EtO)₂CHCH(NHCOCHBrPh)CO₂H and after 3 h., the mixt. was poured over crushed ice, extd. with CHCl₃, washed with aq. NaHCO₃, dried by passage through acid-washed Al₂O₃, and the filtrate was evapd., yielding 4.8 g. oily 2-benzylidene-4-(diethoxymethyl)pseudo-5-oxazolone, which failed to condense with XI. In another attempt, (EtO)₂CHCH(NHCOCHClPh)CO₂Me was condensed

with XI to give α -Me α -chlorobenzylpenicilloate (XII).
On treatment of crude XII (5.2 g.) with a mixt. of 10.8 g. pyridine and 35.2 mL. Ac₂O with shaking and cooling, a dark brown gum was formed, which, crystd. from Et₂O at -50°, gave a "dehydropenicillin" (XIII), C₁₆H₁₆O₄N₂S, m. 90-5° (decompn.).
Addnl. information in printed abstr.

CC 10 (Organic Chemistry)

L36 ANSWER 31 OF 32 HCA COPYRIGHT 2004 ACS on STN

48:40443 Original Reference No. 48:7242c-d Fertilizer. (Council of Scientific and Industrial Research). IN 47439 19540113
(Unavailable). APPLICATION: IN .

AB Kossier phosphate rock contg. 30.8% P₂O₅ and 100 g. of 13.7% CaCO₃ is treated with 142 g. of com. HCl (27% strength). The temp. developed during the reaction is sufficient for the disintegration of the phosphate rock and is maintained for 1 hr. with **mech. agitation**. (NH₄)₂SO₄ (7 g.) is then added to the slurry thus obtained, and the mixt. is **stirred** by mech. means. The mass is then cured by dumping for 3 weeks. After this period 300 g. of a dry mass is obtained which is finally ground to a coarse powder. The product is a mixed N-P fertilizer and contains 15% P₂O₅ and 7.4% N.

CC 15 (Soils and Fertilizers)

L36 ANSWER 32 OF 32 HCA COPYRIGHT 2004 ACS on STN

41:30992 Original Reference No. 41:6189g-i, 6190a-i, 6191a-i, 6192a-c New transformation of crotonaldehyde. Flaig, Wolfgang Reichsamt Wirtschafts-ausbau, Chem. Ber., Prof. Nr. 093(PB52020), 1073-1108 (Unavailable) 1942. OTHER SOURCES: CASREACT 41:30992.

AB Derivs. of the enol form of MeCH:CHCHO were made by the dealkoxylation of acetals and condensation of the alkoxybutadiene with maleic anhydride and phthalic anhydride. MeCH:CHCHO (900 cc.) was added dropwise with stirring in 1.5 hrs. at not over -5° to 300 g. fused Na₂SO₄ in 1800 cc. abs. EtOH satd. with dry HCl. The lower layer was sepd., dried over Na₂SO₄, and distd., b₁₄ 72-4°. Abs. EtOH (1/3 vol.) was added to the distillate, the mixt. was cooled in an ice bath, 150 g. Ca(OH)₂ added immediately, and 200-300 cc. Et₂O at room temp. MeCHClCH₂CH(OEt)₂, b₁₂ 71°, obtained from the filtrate (yield 37%), refluxed 1 hr. with pulverized KOH in a Cu flask, gave 80% MeCH:CHCH(OEt)₂ (I), b₁₇ 49°. Abs. EtOH (3000 g.), 75 g. concd. H₂SO₄, and 1500 g. MeCH:CHCHO was **stirred** 16 hrs. at 50° under a CO₂ atm. NaOH (61 g.) in as little H₂O as possible was added, and a **mixt.** of EtOH, MeCH:CHCHO, and H₂O was distd. off at 40° and 90 mm. The filtrate was fractionated to yield 200 g. MeCH(OEt)CH₂CHO, b₁₄ 40-70°, and 1300-1500 g. MeCH(OEt)CH₂CH(OEt)₂ (II), b₁₄ 80-1°. A condensation product (300 g.) of MeCH:CHCHO remained as a still residue. II, further

purified by refluxing and stirring with powd. KOH in a Cu flask, had d_{420} 0.8750, n_{D20} 1.40429, n_{B20} 1.41105, n_{Y20} 1.41455, n_{D20} 1.40620, and could be kept unchanged by adding a few drops of piperidine. A concd. aq. soln. contg. 40 g. NaOH was added at not over 20° to 1000 g. MeCH:CHCHO, 50 g. concd. H₂SO₄, and 1400 g. MeOH, and the filtrate was distd. at atm. pressure to remove 1000 g. of a **mixt.** of MeCH:CHCHO, MeOH, and MeCH(OMe)CH₂CHO. Distn. of the upper layer of the remaining liquid gave 900-950 g. crude MeCH(OMe)CH₂CH(OMe)₂, which after purification by shaking with aq. NaHSO₃, washing with dil. NaOH, H₂O, drying over KOH, and distn., b_7 44°, d_{420} 0.9180, n_{D20} 1.40073, n_{B20} 1.40735, n_{Y20} 1.41083, n_{D20} 1.40268. Catalysts for dealkoxylation of acetals were made from NaH₂PO₄·2H₂O, Al₂(SO₄)₃·18H₂O, and MgSO₄·2H₂O by heating them until they had dissolved in their water of hydration, then until they had a doughlike consistency, passing them through a 2-mm. sieve to obtain granules, and heating at 350° and 15 mm. to completely remove the H₂O. Catalysts contg. silicates were made by admixt. with 40°B. act. e. water glass and drying 2.5 hrs. at 200°. Activated silica gels were prepd. by treating 45 g. of silica gel with 20 cc. of a 3% soln. of Ni(NO₃)₂, AlCl₃, (NH₄)₂MoO₄, TiCl₃, or MnSO₄ and drying in an oven 1 hr. at 200-50°. A small-scale app. for the conversion of trialkoxybutanes to alkoxybutadiene consisted of a 50-100 cc. heated Claisen flask equipped with dropping funnel, N inlet, manometer, and side arm delivering into an electrically heated tube 2.3 cm. in diam. packed for 30 cm. of its length with the catalytic agent. In 1 hr., 100 g. starting material could be swept through at 250-350° at a pressure difference of 15-20 mm. and condensed in receivers cooled in dry ice-Me₂CO and in liquid air. A larger-scale app. somewhat similar in design permitted the conversion of 1 kg. or more of the starting material at the same rate. The alkoxybutadiene was recovered by washing the contents of the cooled receivers, drying over KOH, and distg. at 40 mm. Variation in catalyst (g.), temp., and time (hrs.) gave the following yields (%) of CH₂:CHCH:CHOEt (III) from 100 g. I and II, resp.: I, 60 NaH₂PO₄, 350°, 1.5, 81; 50 Al₂(SO₄)₃, 300-50°, 45, 52; 60 MgSO₄, 350-70°, 1.5, 59; 35 B₂O₃, 350°, 1, 45. II, 50 Al₂(SO₄)₃, 350°, 1.5, 3.0; 62 B₂O₃P₂O₅, 250°, 1.1, 56; 66 NaH₂PO₄, 320°, 2.5, 65; 69 SiO₂ gel, 200°, 1.3, 56; 48 MgHPO₄-water glass, 350°, 1.1, 74; 35 AlPO₄-water glass, 300°, 1.0, 82; 30 fuller's earth, 300°, 0.6, 37; 10 Al₂O₃, 350°, 1.6, 69; 34 Al₂O₃-water glass, 350°, 1.0, 35; 25 C, 350°, 1.6, 72. MeCH:CHCH(OMe)₂ (100 g.) passed over NaH₂PO₄ in 40 min. at 350° and 18 mm. gave 5 g. forerun, b_{87} 29°, 24 g. CH₂:CHCH:CHOMe, b_{87} 44-6° (58%), 16 g. intermediate fraction b_{87} 48-55°, 27.5 g. MeCH:CHCH(OMe)₂ b_{87} 57°, 2 g. still residue. Approx. the same yield of

CH₂:CHCH:CHOMe was obtained from MeCH(OMe)CH₂CH(OMe)₂ with an activated SiO₂ gel. II (100 g.) and 50 g. Al₂O₃ gave 3.7 g. forerun, b₁₃ 53°, 5.1 g. MeCH(OEt)CH:CHOEt, b₁₃ 60-2°, 26.6 g. II, b₁₃ 76°, and a small amt. of a lower fraction, b. 74-6°. No semicarbazone was obtained from MeCH(OEt)CH:CHOEt but only a p-nitrophenylhydrazone, m. 172-3°, apparently identical with the p-nitrophenylhydrazone of MeCH(OEt)CH₂CHO, m. 172-3°, since a mixed m.p. gave no depression and the mixed m.p. of the p-nitrophenylhydrazone of MeCH:CHCHO (m. 183-4°) and the p-nitrophenylhydrazone of MeCH(OEt)CH:CHOEt was 165-70°. The addn. of 0.1 mole Br during 20 min., with agitation, to 0.1 mole III in 75 cc. abs. Et₂O caused the di-Br compd. to crystallize from soln. Na (0.1 g. atom) in 50 cc. abs. Et₂O was added, the NaBr, EtOH, and Et₂O were removed, and the residue distd. to give 6 g. CH₂BrCH:CHCH(OEt)₂, b_{0.3} 74-5°, d₄₂₀ 1.2424, n_{D20} 1.46997, n_{B20} 1.48159, n_{Y20} 1.48899, n_{D20} 1.47309, a colorless lachrymatory liquid when freshly distd., stable for some days when stored at -20°, rapidly decomp. at room temp. in air. On heating with K₂CO₃, 1 mole EtOH was evolved and the product crystd. at -4°. Br (0.2 mole) was added to 0.1 mole III in 100 cc. Et₂O during 0.75 hr. at -70°, the Et₂O was removed, the residue, needles m. above 30°, was again dissolved in Et₂O, treated with 0.1 g.-atom Na in 50 cc. EtOH, and allowed to stand 20 hrs. at room temp. The NaBr, Et₂O, and EtOH were removed, and somewhat impure CH₂BrCHBrCHBrCH(OEt)₂, b. 92-3° under very low pressure, was obtained. Bromosuccinimide (0.5 mole) was added in a finely powd. and carefully dried state to a vigorously **stirred** soln. of 0.1 mole III in 100 cc. abs. EtOH during 20-30 min. at 0-5°. After stirring 2 hrs. at room temp., the succinimide, EtOH, and Et₂O were removed and by fractionation 64% CH₂BrCH:CHCH(OEt)₂, b_{0.001} 47-51°, d₄₂₀ 1.2378, n_{D20} 1.46884, n_{B20} 1.48064, n_{Y20} 1.48743, n_{D20} 1.47237, was obtained. CH₂BrCH:CHCH(OEt)₂ (42 g.) was slowly added to 122. KOH in 50 cc. MeOH at 0°. The mixt. was warmed 15 min. on the water bath, the KBr filtered off, and 5 vols. H₂O added. The sepd. ethoxy acetal, washed with H₂O, dried over KOH, and distd., gave 65% EtOCH₂CH:CHCH(OEt)₂, b₁ 52°, d₄₂₀ 0.9168, n_{D20} 1.42512, n_{B20} 1.43344, n_{Y20} 1.43781, n_{D20} 1.42759. EtOCH₂CH:CHCH(OEt)₂ (25 g.), vaporized over 20 g. SiO₂ gel in the small-scale app. at 250° and 14 mm., gave 11 g. of what was apparently EtOCH:CHCH:CHOEt, b₄ 52-4°. The originally colorless substance rapidly darkened and only a mol.-wt. detn. could be used to characterize it (found 154, calcd. 142). Methylene blue and other oxidation-reduction indicators were found to direct the reaction between an alkoxybutadiene and maleic anhydride to condensation and to inhibit the heteropolymerization which predominated in the absence of the catalyst. On heating 5 g. III

and 5 g. maleic anhydride in 100 cc. thiophene-free C₆H₆, in the absence and in the presence resp., of 1 mg. methylene blue, the % C₆H₆-insol. resin, C₆H₆-sol. resin, and cyclic addn. product (3-ethoxy-1,2,3,6-tetrahydrophthalic anhydride (IV), m. 38°) formed were: 10,0;40,14;40,84. IV was dissolved in dil. NaOH, the alk. soln. was acidified, extd. with Et₂O, the Et₂O soln. was dried, and the Et₂O removed to yield 3-ethoxy-1,2,3,6-tetrahydrophthalic acid, m. 139-40° (xylene); the di-Me ester, obtained with CH₂N₂, m. below room temp., b₁₄ 120-1°. The effect of the addn. of 2 mg. of catalyst on the yield of IV from 10 g. III and 10 g. maleic anhydride was detd. In 100 cc. Et₂O and in 100 cc. Me₂CO soln., resp., the % yield was as follows: no catalyst, 20, 43; alizarin, 30, 55; anthraquinone, 19, 56; Bismarck Brown R, 39, -; crystal violet (carbinol base), 40, -; 2, 6-dichlorophenol-indophenol, 65, 92; dimethylnaphthoquinone, 31, -; fluorescein, 27, -; hydroquinone, -, 92; Indanthrene Blue B.C.S., 33, -; indanthrene khaki, 19, -; indigo disulfonate, -, 77; indigo trisulfonate, 32, 47; indigo tetrasulfonate, -, 67; indigotin, 28, 56; malachite green, 50, -; methylene blue (cryst.), 84, 76; Methylene Blue B Extra Merck, 65, 70; 1,4-naphthoquinone, 49, -; 1,2-naphthoquinone, 70, -; neutral red, 54, 85; phenanthrenequinone, 57, -; pyrogallol, 65, 85; Safranin T, 63, 77; thionine, 32, 94; thymol-indophenol, -, 70; toluylene blue, 45, 93. No relation was found between oxidation-reduction potential and the relative effectiveness of the catalyst. EtOCH:CHCH:CHOEt (43 g.), 3.1 g. maleic anhydride, and 2 g. methylene blue in 50 cc. thiophene-free C₆H₆ heated 3 hrs. on the water bath yielded 3 g. 3,6-diethoxy-1,2,3,6-tetrahydrophthalic anhydride, b. 126° at a very low pressure, a viscous oil which soon crystd., m. 91° (Et₂O-petr. ether), converted to o-C₆H₄(CO)₂O on heating at atm. pressure. 3-Methoxy-1,2,3,6-tetrahydrophthalic anhydride, m. 105° (from EtOAc), was obtained from the reaction at 125° of 10 g. CH₂:CHCH:CHOMe, 10 g. maleic anhydride, 30 cc. (ClCH₂CH₂)₂O. CH₂:CHCH:CHOAc (57 g.) in 500 cc. C₆H₆ was added at once to 50 g. maleic anhydride in 500 cc. boiling C₆H₆ and the mixt. was heated 1.5 hrs. An insol. resin (7.7 g.) was sepd., 55 g. 3-acetoxy-1,2,3,6-tetrahydrophthalic anhydride (V), m. 58° (from Et₂O), and 10.5 g. residue were obtained on distn. of the C₆H₆ soln. A similar expt. but in which 10 mg. methylene blue was present in the maleic anhydride soln. in C₆H₆ before the CH₂:CHCH:CHOAc was added gave 7 g. resin and 71.5 g. (68.5%) V. V was also prepd. more directly from MeCH:CHCHO. Ac₂O (660 g.), 350 g. MeCH:CHCHO, and 300 g. NaOAc were refluxed 5 hrs. at 160°. The distillate of the resulting filtrate (crude CH₂:CHCH:CHOAc), 0.2 g. thionine, 100 g. maleic anhydride, and 200 cc. Me₂CO were warmed 0.5 hr. on the water bath, and the lower-boiling material was removed at a bath temp. of 70° at 10 mm. pressure. V was obtained from the residue in 95% yield, based on maleic anhydride. Crude CH₂:CHCH:CHOAc, thionine, maleic

anhydride, and Me₂CO contg. 1 g. anhyd. NaOAc treated in a similar manner gave 25-35 g. (70-5%) 3,6-dihydrophthalic anhydride, b0.001 135°, m. 148°, converted to 3,6-dihydrophthalic acid, m. 150-3° (decompn.). 3,6-Dihydrophthalic anhydride was also obtained in almost quant. yield by heating 20 g. V in 5 cc. C₅H₅N 10 min. on the steam bath. 2,3-Dihydrophthalic acid (35 g.), m. 180°, was obtained by refluxing 50 g. V with 40 cc. concd. HCl, and was converted almost quantitatively by Ac₂O to 2,3-dihydrophthalic anhydride, m. 102°. V (42 g.) and 20 g. maleic anhydride were heated in a distg. flask to 200° to remove 11 g. AcOH. Crystals of 3,6-endo-vinylene-1,2,3,4-cyclohexane tetracarboxylic acid anhydride, m. 358° (decompn.), were obtained from the residue by washing with EtOAc; yield 20%. 23 references.

CC 10 (Organic Chemistry)

IT 1303-86-2, Boron oxide, B₂O₃

(as catalyst alone and with P₂O₅ in dealkoxylation of acetals)

IT 1314-56-3, Phosphorus oxide, P₂O₅

(catalysts from B₂O₃ and, in dealkoxylation of acetals)

=> d 137 1-37 ti

L37 ANSWER 1 OF 37 HCA COPYRIGHT 2004 ACS on STN

TI Flux method for manufacturing potassium phosphate titanate single crystal with suppressed flux inclusion

L37 ANSWER 2 OF 37 HCA COPYRIGHT 2004 ACS on STN

TI Bitumen modified with phosphorous compounds and a propylene polymer composition

L37 ANSWER 3 OF 37 HCA COPYRIGHT 2004 ACS on STN

TI Preparation of hydroxyapatite as stabilizer for suspension polymerization

L37 ANSWER 4 OF 37 HCA COPYRIGHT 2004 ACS on STN

TI Dispersants of antimony oxides and their compositions

L37 ANSWER 5 OF 37 HCA COPYRIGHT 2004 ACS on STN

TI Insoluble cyclodextrin polymer beads

L37 ANSWER 6 OF 37 HCA COPYRIGHT 2004 ACS on STN

TI Purification of sodium hexafluorosilicate

L37 ANSWER 7 OF 37 HCA COPYRIGHT 2004 ACS on STN

TI Clathrating anion-exchange resin

- L37 ANSWER 8 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Clathrating cation-exchange resin
- L37 ANSWER 9 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Ammonium phosphate compositions suitable for granular fire extinguishers
- L37 ANSWER 10 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Treating used motor oil and synthetic crude oil
- L37 ANSWER 11 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Treating used industrial oil
- L37 ANSWER 12 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Ferric oxide-zinc oxide pigment
- L37 ANSWER 13 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Low-halogen zinc ferrite pigments and their use
- L37 ANSWER 14 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Phosphate ion absorbent
- L37 ANSWER 15 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Filled unsaturated polyester resin compositions
- L37 ANSWER 16 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI A process for dephosphorizing molten pig iron
- L37 ANSWER 17 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Storage-stable, granulated silage additives
- L37 ANSWER 18 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Dephosphorizing molten pig iron
- L37 ANSWER 19 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Study of the decomposition kinetics of Karatau phosphorite fines by nitric acid and the rate of pulp filtration under pilot-plant conditions
- L37 ANSWER 20 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Refining of steelmaking slag
- L37 ANSWER 21 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Effect of the lump sizes of lime on its accumulation in the slag
- L37 ANSWER 22 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Treatment of anatase ore

- L37 ANSWER 23 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Manufacture of sodium tripolyphosphate
- L37 ANSWER 24 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Peptides. LXXIII. Synthesis of the A chain of sheep insulin with exclusive use of acid labile protective groups
- L37 ANSWER 25 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Mullite production
- L37 ANSWER 26 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Converting crude siliceous bauxite to mullite
- L37 ANSWER 27 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Flame-retardant polyurethane foams
- L37 ANSWER 28 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Fly ash as a coagulant aid in water treatment
- L37 ANSWER 29 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Pituitary growth hormone promoter
- L37 ANSWER 30 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Colorimetric determination of arginine in protein acid hydrolyzates obtained from wheat flour
- L37 ANSWER 31 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Isolation and characterization of soluble ribonucleic acid (RNA) from brewers' yeast
- L37 ANSWER 32 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Chemical fertilizer
- L37 ANSWER 33 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Proximity effects. XIX. Solvolysis of 4-cycloocten-1-yl brosylate with trifluoroacetic acid
- L37 ANSWER 34 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Degradative studies on fucoidin
- L37 ANSWER 35 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Assay of insulin in vitro by fibril elongation and precipitation
- L37 ANSWER 36 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI The preparation and properties of equine pituitary gonadotropin
- L37 ANSWER 37 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Nucleic acids. II. Nucleotidase from intestinal mucosa

=> d 137 17 cbib abs hitind

L37 ANSWER 17 OF 37 HCA COPYRIGHT 2004 ACS on STN

88:188524 Storage-stable, granulated silage additives. (Guano-Werke A.-G., Fed. Rep. Ger.). Belg. BE 852698 19770921, 12 pp. (French). CODEN: BEXXAL. APPLICATION: BE 1977-175969 19770321.

AB A granulated, noncaking silage additive contg. urea [57-13-6] and phosphates and some chlorides of Ca, Mg, and Na is manufd. by reacting a mixt. of urea and oxides and hydroxides and (or) carbonates of Mg, Ca, and Na, screening the product, and spraying with H₃PO₄ while mixing to form phosphates, which leave the mixer in the form of moist granules. For example, in the continuous app. described were ground, each h, 5000 kg recycled product screenings (<0.5 mm and >2.0 mm), 2540 kg urea (46% N), 170 kg dolomitic limestone (32.2% Ca, 19.5% Mg), 48 kg Ca(OH)₂, 650 kg CaCO₃, and 75 kg trace element mixt. The powd. mixt. was transported to a granulating drum rotating at 5 rpm, in which the mixt. was violently **stirred**. H₃PO₄ (50% **P205**) was sprayed at 1215 kg/h and then 50% NaOH was sprayed at 465 kg/h. The exothermic reaction provided an equil. temp. of 60° in the mixing area; the product with H₂O content of 8% was dried to 4% at 90-110° and, the dried granules were screened and the fines recycled. The compn. of the product was: N (urea) 24.3, **P205** 12.1, H₂O-sol. **P205** 6.0, Ca 11.4, Mg 0.7, and Na 2.7%; the pH of a 10% aq. suspension was 7.0, and granule size was 0.5-2.0 mm.

IC A01N

CC 17-5 (Foods)

=> d 138 1-46 ti

L38 ANSWER 1 OF 46 HCA COPYRIGHT 2004 ACS on STN

TI Manufacture of glass by stirring of molten glass by magnetic field

L38 ANSWER 2 OF 46 HCA COPYRIGHT 2004 ACS on STN

TI Glass-forming gel-coated pigments in printing pastes for enameling glass substrates, and their manufacture

L38 ANSWER 3 OF 46 HCA COPYRIGHT 2004 ACS on STN

TI Phosphoric ester surfactants for granular or **flowable** pesticide formulations

L38 ANSWER 4 OF 46 HCA COPYRIGHT 2004 ACS on STN

TI Iron- and lithium-promoted catalysts for the production of maleic anhydride

- L38 ANSWER 5 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Conductive polymer with naphthothiophene structure
- L38 ANSWER 6 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Silane production
- L38 ANSWER 7 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Unsaturated acids and esters
- L38 ANSWER 8 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Gelling agents for hydrocarbon compounds
- L38 ANSWER 9 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Oxygen steel-smelting from pig iron of low phosphorus and sulfur contents
- L38 ANSWER 10 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Storable and **flowable** long-chain alkyl phosphates
- L38 ANSWER 11 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Phosphoric acid preparation by the Fison process
- L38 ANSWER 12 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Apparatus comprising **stirred** reactor vessels for making phosphoric acid
- L38 ANSWER 13 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Increasing available phosphate content of phosphate ore, for use as fertilizers
- L38 ANSWER 14 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Terpenoids. XXVIII. Synthesis of humbertiol
- L38 ANSWER 15 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Ammonium phosphate slurry fertilizer production by a continuous process
- L38 ANSWER 16 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Pyridoxal 5'-orthophosphate
- L38 ANSWER 17 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Polymerization of propylene in the presence of a Ziegler catalyst, water, and an amine
- L38 ANSWER 18 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Composite fertilizer from phosphate, nitric acid, ammonia, and sulfur dioxide

- L38 ANSWER 19 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Studies on peptides. VIII. Synthesis of two heptapeptides isolated from pituitary glands
- L38 ANSWER 20 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Perfluorodecalin and octafluorodecalin synthesis
- L38 ANSWER 21 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Pulplike fertilizers
- L38 ANSWER 22 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Photosensitized oxygen transport to (+)-3-carene
- L38 ANSWER 23 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Infrared absorbent aluminum phosphate coatings and method of manufacture
- L38 ANSWER 24 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Fermentation of waste water from the brown-coal industry
- L38 ANSWER 25 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI N-Methylol amide derivatives
- L38 ANSWER 26 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Spectrophotometric determination of submicro quantities of ajmaline
- L38 ANSWER 27 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Bridged polycyclic compounds. XXII. Carbenoid decomposition of nortricyclenone p-toluenesulfonylhydrazone
- L38 ANSWER 28 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Nucleic acid components and their analogs. XIX. Synthesis of 3-methyl-6-azauridine 5'-phosphate and pyrophosphate
- L38 ANSWER 29 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Vapor-phase fluorination of trichloroethylene with cobalt trifluoride and with manganese trifluoride
- L38 ANSWER 30 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Ammonium citrate-soluble phosphate fertilizers containing mostly anhydrous dicalcium phosphate
- L38 ANSWER 31 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Alkaline degradation of guaran and characterization of "β"-D-isosaccharinic acid
- L38 ANSWER 32 OF 46 HCA COPYRIGHT 2004 ACS on STN

- TI Improving the **flow** properties of highly ammoniated processed phosphate mixtures for multnutrient fertilizers
- L38 ANSWER 33 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Polymerization reactions of itaconic acid and its derivatives
- L38 ANSWER 34 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI The preparation of D-ribose-1-C14, D-arabinose-1-C14, and D-2-deoxyribose-1-C14
- L38 ANSWER 35 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Heterocyclic vinyl eters. XVI. 2,5 Dimethyl-1,4-dithiadine
- L38 ANSWER 36 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Fluorinated carbon compounds
- L38 ANSWER 37 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Pyrimidine nucleoside phosphates
- L38 ANSWER 38 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Cyclopropene. I. The reaction of 2-bromocyclopropanecarboxylates with potassium tert-butoxide
- L38 ANSWER 39 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Mechanism of fluorination. I. Fluorine sensitized oxidation of trichloro- and tetrachloroethylene
- L38 ANSWER 40 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Grignard reagents of sulfones. III. Preparation and properties
- L38 ANSWER 41 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI The controlled thermal decomposition of cellulose nitrate. I
- L38 ANSWER 42 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Mechanism of oxidation. X. The conversion of tetrahydroharman alkaloids into derivatives of linear pyrroquinolones
- L38 ANSWER 43 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Phosphate fertilizers
- L38 ANSWER 44 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI 4-Benzyl-2,6-dimethylpyridine, 1-benzylisoquinoline, 9-benzylacridine, and certain relatives
- L38 ANSWER 45 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Aluminum-alloy method for the gravimetric determination of total oxygen in plain carbon steels

L38 ANSWER 46 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Preparation of chlorine heptoxide

=> d 138 3,10,32 cbib abs hitind

L38 ANSWER 3 OF 46 HCA COPYRIGHT 2004 ACS on STN

108:217810 Phosphoric ester surfactants for granular or **flowable** pesticide formulations. Girardeau, Yvette; Ruffo, Georges; Segaud, Christian (Rhone-Poulenc Chimie SA, Fr.). Eur. Pat. Appl. EP 252824 A1 19880113, 29 pp. DESIGNATED STATES: R: AT, BE, CH, DE, ES, FR, GB, GR, IT, LI, LU, NL, SE. (French). CODEN: EPXXDW. APPLICATION: EP 1987-401564 19870703. PRIORITY: FR 1986-10159 19860711.

AB The surfactants comprise mixts. of alkoxyated phosphoric monoesters R1OROP(O)(OH)2 (I) and phosphoric diesters (R1ORO)2P(O)(OH)(II) [OR = C2-4 oxyalkylene moieties (1-80 repeating units); R1 = C8-20 alkyl or alkenyl, Ph, alkylphenyl, CHR4Ph; R4 = H, Ph, C1-4 alkyl]. The molar II/I ratio is ≥ 0.9 . I + II represents $\geq 1\%$ (molar) of the surfactant, the balance being the alkoxyated alc. R1OROH. **Stirred** 3 mol R2OROH was treated continuously (1h 15 min) with 1 mol **P2O5** at 43°, followed by stirring for 30 min and neutralization (pH 8) with triethanolamine to give a surfactant. Six g surfactant in 19.5 g monoethylene glycol was treated with 0.3g antifoam agent 416/R, 115.2 g water and 135 g plictran. The mixt. was processed in a ball mill and treated with 24 g 2% aq. Rhodopol 23, to give a **flowable** formulation.

IC ICM B01F017-00

ICS C07F009-09; A01N025-30

CC 5-6 (Agrochemical Bioregulators)
Section cross-reference(s): 46

L38 ANSWER 10 OF 46 HCA COPYRIGHT 2004 ACS on STN

77:164019 Storable and **flowable** long-chain alkyl phosphates. Roszinski, Hilmar; Klose, Werner; Noelker, Dieter (Knapsack A.-G.). Ger. Offen. DE 2114145 19721005, 9 pp. (German). CODEN: GWXXBX. APPLICATION: DE 1971-2114145 19710324.

AB Title compds. contg. 1.1-7.2:1 (HO)2P(O)OR (I)-HOP(O)(OR)2 (II) (R = n-C18H37 or mixts. of n-C16H33, n-C18H37, and n-C20H41) were prepd. and made storable by solidification of the molten mixts. with simultaneous scaling, keeping the scaly product .apprx.1 hr at >20° below the m.p., and controlling bulk height 5-12 cm, e.g. in a fluidized bed. Thus, **P2O5** was added to molten n-C18H37OH (III) at 90° and the mixt. **stirred** 5 hr at this temp. to give a 1.1:1 I-II mixt. (R = n-C18H37) contg. 4.4 III and 0.3 H3PO4. This mixt. was heated at 80°, scaled, and the scaly product passed 1 hr at $\leq 50^\circ$ and bulk height .apprx.5 cm through a rotating open tube to give storable scaly

product.

IC C07F
CC 23-8 (Aliphatic Compounds)
IT 112-92-5 629-96-9 36653-82-4
(reaction of, with **phosphorus pentoxide**)

L38 ANSWER 32 OF 46 HCA COPYRIGHT 2004 ACS on STN

55:133435 Original Reference No. 55:25134f-i Improving the **flow** properties of highly ammoniated processed phosphate mixtures for multinutrient fertilizers. Karbe, Kurt; Boos, Wilhelm (Gewerkschaft Victor). DE 973443 19600218 (Unavailable). APPLICATION: DE .

AB Phosphate-HNO₃ mixts. retain good **flow** properties during neutralization and subsequent treatment with NH₃ and CO₂ if 20-50% KCl (based on the amt. of crude phosphate) is added at pH 4-5. Only a fraction of the normally added amt. of stabilizer, esp. MgSO₄, is necessary to ensure citrate soly. of the phosphate if KCl contg. MgSO₄ is added. Thus, 25 kg. Morocco phosphate (33.4% **P2O5**) was processed with 34 l. of 52% HNO₃. The liquid mass was treated with 2.88 kg. MgSO₄. 7H₂O (0.20 mole MgO/mole **P2O5**), neutralized (pH 7.5) with NH₃, and treated with CO₂ and NH₃ at 60°. The mass became stiff and could not be **stirred**. Less than 1% CO₂ was taken up. If the mass was only neutralized to pH 4.5, treated with 10 kg. KCl (59% K₂O), treated with more NH₃ to give pH 7.5, and treated with CO₂ and NH₃ at 60°, the mass remained a mobile liquid and contained finally N (total) 10.80, **P2O5** (total) 9.01, **P2O5** (citrate-sol.) 8.86, H₂O 20.0, K₂O 6.5, CO₂ 3.55, and MgO 0.6%. The mixt. was treated with 30 kg. of 40% KCl, mixed with 3 times the amt. of previously dried material, and granulated to give a fertilizer contg. N 10.1, **P2O5** 8.18, **P2O5** (citrate-sol.) 8.05, and K₂O 18.14%. In a similar example, no MgSO₄.7H₂O was used, and 6 kg. 59% KCl contg. 0.8% MgO was added to give a content of 0.020 mole MgO/mole **P2O5**. The final liquid mass contained N 11.7, **P2O5** 9.78, **P2O5** (citrate-sol.) 9.70, H₂O 25.3, MgO 0.05, and CO₂ 3.40%.

NCL 16
CC 15 (Soils and Fertilizers)
IT Fertilizers
(ammoniated carbonated HNO₂-treated phosphate, **flow** control in making, by KCl)

=> d 139 1-15 ti

L39 ANSWER 1 OF 15 HCA COPYRIGHT 2004 ACS on STN

TI Device for reduction of iron and vanadium in phosphoric acid solution

- L39 ANSWER 2 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Glass preform for optical fibers
- L39 ANSWER 3 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Catalytic oxidation of asphalt
- L39 ANSWER 4 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Granular catalysts and catalyst supports
- L39 ANSWER 5 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Separating solids suspended in a liquid
- L39 ANSWER 6 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Ammoniated phosphoric acid
- L39 ANSWER 7 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Gelatination during the decomposition of apatite by phosphoric acid
- L39 ANSWER 8 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Granulation of mixed complex fertilizers
- L39 ANSWER 9 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Specialized x-ray quantometer for the analysis of coarse-grained samples. Design of the quantometer model and certain results from the preliminary tests
- L39 ANSWER 10 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Free-flowing fertilizer
- L39 ANSWER 11 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI High analysis ammonium polyphosphate fertilizer
- L39 ANSWER 12 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Granular diammonium phosphates
- L39 ANSWER 13 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Sodium tripolyphosphate
- L39 ANSWER 14 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Comparative consideration on metallurgical behavior of high-temperature coke from brown coal
- L39 ANSWER 15 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Polymerization of isobutylene. II. Action of acid iron phosphates on a carrier

=> d 139 5,6 cbib abs hitind

L39 ANSWER 5 OF 15 HCA COPYRIGHT 2004 ACS on STN

79:7130 Separating solids suspended in a liquid. (Tate and Lyle Ltd.).
Fr. Demande FR 2143201 19730309, 29 pp. (French). CODEN: FRXXBL.
APPLICATION: FR 1972-22375 19720621.

AB Sugar juice, liquor, or syrup were clarified by a multi stage process involving addn. of a cationic surfactant as the primary flocculant, phosphatation-flotation during refining of the sugar, and addn. of an anionic flocculant based on polyacrylamide (I) (Taloflote) [9003-05-8], sepg. the secondary flocculated material by flotation, and clarifying the treated liquor by flocculation of the primary solid material contg. the coloring matter. Thus, to Jamacian sugar refusion liquor entering at **flow** rate 500 ml/min at 65.deg. Brix and 80.deg. was added phosphoric acid and lime to form the primary phosphate flocculant. Several samples with various concns. of **P2O5** from 100-600 ppm based on sugar solids were obtained. A control sample was also obtained before the phosphoric acid addn. The liq. was aerated by an agitator with diam. 0.91 m turning at 6000 **rpm**, and 10 ppm (based on sugar solids) I was added to give 0.1g flocculant/100 ml soln. After holding the liquor in the flocculator for a sufficient time, it was transferred to the separator and finally to the defecator to give **P2O5** 300 ppm, attenuation index 978, color after filtration through Millipore 973, turbidity index 0, and decoloration 33%, compared with 0, 2308, 1467, 841, and 0, resp., for the untreated liquor.

IC B01D; B03D; C13D

CC 44-2 (Industrial Carbohydrates)

L39 ANSWER 6 OF 15 HCA COPYRIGHT 2004 ACS on STN

75:97849 Ammoniated phosphoric acid. Legal, Casimer C., Jr. (W. R. Grace and Co.). Fr. Demande FR 2015048 19700612, 15 pp. (French). CODEN: FRXXBL. PRIORITY: US 19680805.

AB An ammonium phosphate was prepd. by reaction of H3PO4 and NH3 at high temps. in a tubular reactor. The heat of reaction was rapidly dissipated by the tubular reactor design. Thus, H3PO4 and anhyd. NH3 were 1st preheated to 135° before being reacted together in the reactor. The resulting reaction raised the temp. to 204-60°. The reaction product was led into a chamber and agitated with a rotating blade at 350 **rpm**. The NH3 and moisture were removed by a **flow** of air, and recycled. Retention time in the chamber was .apprx.5 min. The product contained 30.6% **P2O5** as polyphosphate which can be suitably used for fertilizer.

IC C01B; C05B

CC 20 (Fertilizers, Soils, and Plant Nutrition)

=> d his 140-

FILE 'HCA' ENTERED AT 15:44:05 ON 10 AUG 2004

L40 37 S L4(3A)L5
L41 1 S L40 AND (L6 OR L7 OR L8)
L42 1 S L40 AND L9
L43 5 S L40 AND L3
L44 0 S L40 AND (L28 OR L29)
L45 163 S L4(3A)(L6 OR L7 OR L8)
L46 10 S L45 AND L3
L47 3 S L45 AND L5
L48 0 S L45 AND (L28 OR L29)
L49 4 S L3(3A)L5
L50 2 S L3(3A)(L6 OR L7 OR L8)
L51 18 S (L41 OR L42 OR L43 OR L46 OR L47 OR L49 OR L50) NOT L36

=> d 151 1-18 cbib abs hitind

L51 ANSWER 1 OF 18 HCA COPYRIGHT 2004 ACS on STN

127:96616 Preparation and use of granular black iron oxide pigments. Koehler, Berndt-Ullrich; Eitel, Manfred; Linde, Guenter; Kunstmann, Herbert (Bayer A.-G., Germany). Ger. Offen. DE 19548418 A1 19970626, 5 pp. (German). CODEN: GWXXBX. APPLICATION: DE 1995-19548418 19951222.

AB The title pigments, stable and universally useable, are prepd. by adding 0.1-1.6% (based on oxide) binder to an Fe₃O₄ dispersion, drying, granulating, and heating at 80-650° in an inert or slightly reducing or oxidizing atm. A 40-70% Fe₃O₄ pigment paste was **stirred** with 1.0% P₂O₅ (from Na polyphosphate) at room temp., spray dried, and heated under N in a rotary furnace at 400° for 30-60 min to give a pigment with relative (to Bayferrox 330) dispersibility 103%, coloristic values relative F 98% and b* -1.8, oxidn. stability (IMCO) 150°, and Fe(III)-Fe(II) ratio 1.9:1.

IC ICM C09C001-24

ICS C01G049-02; C04B014-36; C04B040-00; C09D017-00; C08K003-22

ICA C08J003-20

CC 42-6 (Coatings, Inks, and Related Products)

IT 1314-56-3, **Phosphorus pentoxide**, uses

7631-86-9, Silica, uses

(binder; **prepn.** and use of granular black iron oxide pigments)

L51 ANSWER 2 OF 18 HCA COPYRIGHT 2004 ACS on STN

126:134471 Generation and relaxation of flow birefringence of high-viscous alkali phosphate glass melts. Brueckner, Rolf; Murach, Juergen; Hao, Shen (Institut fuer Nichtmetallische Werkstoffe, TU Berlin, Berlin, Germany). Journal of Non-Crystalline Solids,

208(3), 228-236 (English) 1996. CODEN: JNCSEBJ. ISSN: 0022-3093.
Publisher: Elsevier.

- AB It will be shown that there is a remarkable difference between the generation and relaxation behavior of the flow birefringence of alkali phosphate melts which is assumed to be in close connection to the stress relaxation modulus and to the recently defined stress generation modulus. This behavior is investigated under isothermal conditions within the high-viscosity range between 108 and 1012 Pa s by means of loading and unloading ternary sodium-lithium phosphate glass rods. The evaluation of the optical birefringence during loading and unloading exhibits two different generation and two relaxation times during the two processes in contrast to earlier investigations within the low-viscosity range <107 Pa.s where only one relaxation time was obsd. This result is in agreement with the structural conception of chains with increasing length and entanglement with decreasing temp. The dependence of the relaxation times on the chem. compn. has a max. at 50 mol% P2O5. The decrease of the relaxation times towards higher phosphate concns. points out a beginning of cross-linkage while towards lower phosphate concns. the length of the PO4-chains seems to be reduced. Of special interest is that the generation time is smaller than the relaxation time and decreases with increasing stress while the relaxation time increases with increasing stress. This behavior appears to be connected to orientation effects and to typical non-Newtonian flow (shear thinning effect).
- CC 57-1 (Ceramics)
- IT 1314-56-3, Phosphorus oxide (P2O5), properties
(glass; **generation** and relaxation of **flow**
birefringence of high-viscous alkali phosphate glass melts)

L51 ANSWER 3 OF 18 HCA COPYRIGHT 2004 ACS on STN
117:212315 Preparation of 2-substituted indoles via Fischer indole **synthesis** using **phosphorus pentoxide**-methane sulfonic acid catalysts. Hughes, David L.; Zhao, Dalian (Merck and Co., Inc., USA). Brit. UK Pat. Appl. GB 2251856 A1 19920722, 48 pp. (English). CODEN: BAXXDU. APPLICATION: GB 1992-653 19920114. PRIORITY: US 1991-642778 19910118.

GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

- AB Title compds. [I; R, R11, R12 = H, halo, alkyl, alkenyl, alkynyl, CF3, cyano, NO2, N3, C(OH)R3R4, CO2R7, SR8, SOR8, SO2R8, SO2N(R9)2, OR9, N(R9)2, COR10, etc.; R1 = R, Q1; R2 = H, XR13; R3-R6 = H, alkyl; CR3R4, CR5R6 = C3-6 cycloalkyl; R7 = H, alkyl, (substituted)

PhCH₂; R₈ = CF₃, alkyl, (substituted) phenyl(alkyl); R₉ = H, COR₁₀, alkyl, (substituted) phenyl(alkyl); R₁₀ = H, CF₃, alkyl, alkenyl, alkynyl, (substituted) Ph (alkyl); R₁₃ = alkyl, alkenyl, (substituted) phenyl(alkyl); X = CO, CR₃R₄, SO₂, bond; Y = O, NR₉, CO, CR₃R₄, S, SO, SO₂; Q = H, CO₂R₇, CONHSO₂R₈, NHSO₂R₈, SO₂NHR₉, CON(R₉)₂, CH₂OH, tetrazolyl; m, v = 0, 1; n = 1-3; p = 0-3], were prepd. by treatment of hydrazone II with a catalyst contg. P2O₅/MeSO₃H (1:2-40) optionally in the presence of a cosolvent. Thus, 1-(4-chlorobenzyl)-1-[4-(2-quinolinylmethoxy)phenyl]hydrazine, MeCOCH₂CMe₂CO₂Me, 4 Å sieves, HOAc, and PhMe were refluxed to give 91% hydrazone, which was **stirred** with P2O₅/MeSO₃H in sulfolane at 45-60° for 5d to give 85% indole III.

IC ICM C07D209-04

CC 27-11 (Heterocyclic Compounds (One Hetero Atom))

IT Fischer indole **synthesis** catalysts

(**phosphorus pentoxide**-methanesulfonic acid)

IT 100-63-0 107-87-9, 2-Pentanone 590-50-1 618-40-6 66372-99-4,
Methyl 2,2-dimethyl-4-oxopentanoate 133165-83-0 133165-84-1
133165-85-2 133165-86-3 133166-03-7 133166-04-8 133166-05-9
133190-96-2

(Fischer indole **synthesis** reaction of,
phosphorus pentoxide-methanesulfonic acid
catalysts in)

IT 133165-87-4P 133165-99-8P
(prepn. and Fischer indole **synthesis** reaction of,
phosphorus pentoxide-methanesulfonic acid
catalysts for)

IT 133166-00-4DP, prepn. of, via Fischer indole **synthesis**,
phosphorus pentoxide-methanesulfonic acid
catalysts for
(prepn. of)

IT 91-55-4P 3484-18-2P 3623-86-7P 19869-53-5P 31151-19-6P
38136-74-2P 59931-85-0P 68051-17-2P 93549-89-4P 133165-90-9P
133165-91-0P 133165-93-2P 133165-94-3P 133165-95-4P
133165-96-5P 133165-97-6P 133165-98-7P 133166-01-5P
(prepn. of, via Fischer indole **synthesis**,
phosphorus pentoxide-methanesulfonic acid
catalysts for)

L51 ANSWER 4 OF 18 HCA COPYRIGHT 2004 ACS on STN

107:97274 Iron- and lithium-promoted catalysts for the production of maleic anhydride. Franchetti, Victoria Marie; Keppel, Robert Andrew (Monsanto Co., USA). Eur. Pat. Appl. EP 221876 A2 19870513, 12 pp. DESIGNATED STATES: R: DE, ES, FR, GB, IT. (English). CODEN: EPXXDW. APPLICATION: EP 1986-870157 19861027. PRIORITY: US 1985-791655 19851028; US 1985-791977 19851028.

AB Maleic anhydride is manufd. by the partial oxidn. of nonarom. hydrocarbons in the presence of a catalyst comprising P, V, O, and a

promoter component contg. Fe and Li. The catalyst has P-V atom ratio 0.50-2.00, (Fe + Li)/V atom ratio 0.0025-0.0080, Fe/V atom ratio 0.0010-0.0040, and Li/V atom ratio 0.0015-0.0040. The catalyst is prepd. by contacting a tetravalent V compd. and a P compd. with the promoter in an anhyd. alc. in the presence of anhyd. HCl to form a catalyst precursor which is dried, roasted, and calcined. A reactor was charged with 901.8 g 85.5% H₃PO₄, the acid stirred, and 343.4 g P₂O₅ added, the soln. **stirred** for 20 min, and cooled to .apprx.20°. A second stirred reactor was charged with 8.3 L iso-BuOH, the alc. cooled to 10-15°, over 12 min the above-prepd. 100% H₃PO₄ added, the mixt. cooled, 963.0 g V₂O₅ stirred in, 1.35 g LiCl added, 0.96 g Fe powder added along with 1.0 L iso-BuOH. Anhyd. HCl (2,037.0 g) was added to the mixt. over a 4.67-h period, the soln. heated to reflux for 2 h, 5.4 L of distillate removed over 5.0 h, the mixt. refluxed for 1.38 h, 1.5 L distillate removed over a 2.36-h period, the turbid mixt. poured into Pyrex cake pans and placed in an oven at 140-150° for 5.5 h producing 2,225.0 g dried catalyst precursor which was ground, sieved, and roasted in a N-purged furnace to 260° over a 1-h period, and roasting continued for 3 addnl. hours, followed by gradual replacement of the N with air, and heating an addnl. 3 h to yield 1,980.0 g of black catalyst precursor powder. The dry powder was mixed with 1% powd. graphite, the mixt. pressed into pellets, and calcined. The catalyst was charged into a tubular reactor, heated to 200°, heated to 250° in **flowing** dry air over a 3.124-h period, the temp. reduced to 230°, and 1.8 vol.% H₂O added to the dry **flowing** air. The reactor temp. was increased to 280° at 3°/h and 0.6 mol.% butane (I) was added to the **flowing** water-contg. air stream. The reactor temp. was increased to 400° at 1°/h and there maintained for 6 h. The catalyst P1.20V1.00Fe0.0015Li0.0030Ox was fed with I at 1.9 h-1 at 413-451°, resulting in I conversion 78.1% with maleic anhydride selectivity 69.8%.

IC ICM C07C051-215

ICS B01J027-198; B01J023-78

CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 27, 67

L51 ANSWER 5 OF 18 HCA COPYRIGHT 2004 ACS on STN

104:209445 Device for reduction of iron and vanadium in phosphoric acid solution. Ressel, Herbert; Westphal, Wilhelm (Hoechst A.-G., Fed. Rep. Ger.). Ger. Offen. DE 3437689 A1 19860417, 9 pp. (German). CODEN: GWXXBX. APPLICATION: DE 1984-3437689 19841015.

AB Fe and V are reduced in phosphoric acid soln. in a rotating drum partially filled with granular reducing agent, with inlets for the H₃PO₄, granular reducing agent, and an inert gas and an outlet for the reaction product, e.g., in the form of an overflow tube from the

top of the drum. Ferrophosphorus, FeSi, Fe oxides, or red P may be used as the granular reducing agent. Thus, a 0.8-m diam., 3-m long drum contg. 6 baffle plates was filled with 1.6 ton broken ferrophosphorus (<10 mm, fine particles <0.5 mm 3.8%, compn. P 22.9, Si 4.7, Ti 2.4%, balance Fe) and rotated at 2 **rpm**, hot H3PO4 (contg. **P2O5** 27.9 wt.%, V5+ 123 ppm, total Fe 0.2 and Fe2+ 0.02%) was fed at 7 m3/h and 80-90° through an inlet with a stopper screw and **flowed** out through the overflow to the bottom of a container with a double-arm stirrer where it reacted with the finely divided ferrophosphorus particles, solids settled out, and the clear liq. was released from the top of the container and collected in a vessel from which a reaction product was removed contg. total Fe 0.23, Fe 2+ 0.22, and V4+ 115 ppm.

IC ICM C01G001-00

ICS C01G031-00; C01G049-00

CC 49-1 (Industrial Inorganic Chemicals)

Section cross-reference(s): 47

L51 ANSWER 6 OF 18 HCA COPYRIGHT 2004 ACS on STN

102:26528 Epoxy phosphoric acid adducts. Lottermoser, Manfred (Fed. Rep. Ger.). Ger. Offen. DE 3304379 A1 19840809, 11 pp. Addn. to Ger. Offen. 3,208,748. (German). CODEN: GWXXBX. APPLICATION: DE 1983-3304379 19830209.

AB Compns. useful in rust conversion, coatings, lubricants, etc. are prepd. by reaction of unsatd. materials (e.g. oils, olefins, polystyrene waste) with peroxides and P2O5. Thus, adding 153 mL 30% H2O2 in portions to 100 g linseed oil and 40.4 g **P2O5** **stirred** at 120-130° gave a viscous, honey-yellow product sol. in aq. alkalies and iso-PrOH. Aq. solns. of alkali or alkanolamine salts were useful in rust prevention, and iso-PrOH solns. were good rust conversion coatings for rusted steel.

IC C07F009-09; C09D005-08; C10M003-40; C10M001-46; B01F017-14; C08K009-04; B05D007-14; B05D007-26; C23F011-16; E04B001-62

CC 42-10 (Coatings, Inks, and Related Products)

IT Corrosion inhibitors

(olefin-hydrogen peroxide-**phosphorus pentoxide** reaction **products** as)

IT Coating materials

(rust-converting, olefin-hydrogen peroxide-**phosphorus pentoxide** reaction **products** as)

IT 111-66-0D, reaction products with hydrogen peroxide and phosphorus pentoxide 143-28-2D, reaction **products** with **phosphorus pentoxide** and hydrogen peroxide 1314-56-3D, reaction **products** with unsatd. compds. and hydrogen peroxide 7722-84-1D, reactions products with olefins and phosphorus pentoxide 13598-52-2D, reaction products with olefins
(anticorrosive compns. contg.)

L51 ANSWER 7 OF 18 HCA COPYRIGHT 2004 ACS on STN

100:88051 Mathematical model of continuous decomposition of potassium chloride with polyphosphoric acid. Kubaev, A. Kh.; Namazov, Sh. S.; Radzhabov, R.; Beglov, B. M.; Kamalov, K. M. (Inst. Khim., Tashkent, USSR). *Uzbekskii Khimicheskii Zhurnal* (6), 59-63 (Russian) 1983. CODEN: UZKZAC. ISSN: 0042-1707.

AB A math. model is developed, on the basis of exptl. studies in 2 graphite reactors connected in parallel, for the decompn. of KCl with polyphosphoric acid. An increase in temp. and concn. of the polyphosphoric acid increases the coeff. of decompn. of KCl. The optimal conditions for the reaction are: temp. 245-250°, concn. of the polyphosphoric acid 76.7% **P2O5** and the mass **flow** rate of KCl at P2O5:K2O ratio of 1:0.5 is 35-45 g/h for a reactor vol. of 2.85×10^{-6} m³. Under these conditions, the coeff. of decompn., concn. of **P2O5** in the **product**, and the degree of conversion of P2O5 are 98.3-98.4, 59.20-59.65, and 79.5-80.1%, resp.

CC 49-10 (Industrial Inorganic Chemicals)

L51 ANSWER 8 OF 18 HCA COPYRIGHT 2004 ACS on STN

89:162274 Preparation of potassium sulfopolyphosphates based on the reaction of potassium chloride with sulfopolyphosphoric acid. Namazov, Sh. S.; Arifdzhonov, S. M.; Adylova, M. R. (Inst. Khim., Tashkent, USSR). *Uzbekskii Khimicheskii Zhurnal* (4), 3-7 (Russian) 1978. CODEN: UZKZAC. ISSN: 0042-1707.

AB Highly-concd. Cl-free P-K fertilizers were obtained by reacting KCl with thermal sulfopolyphosphoric acid (81.56% P2O5) prepd. according to US Patent No. 334005 (1967). Increasing the temp. (100-350°) and the P2O5/K2O ratio (1:0.5, 1:0.668 and 1:0.8) affected significantly the Cl- evolution; it reached 99.75% at 250° and P2O5/K2O ratio 1:0.5. The products of KCl decompn. obtained at the former **P2O5/K2O** ratio **formed** a highly mobile, **flowing** melt easily removable from the reactor when hot. Total P in the products increased and H2O-sol. P decreased at all P2O5/K2O ratios with increasing decompn. temp. In the products 7-8 phosphate forms were found. K sulfopolyphosphate obtained at 200-350° contained trimeta, tetrameta, and pentameta phosphate anions. The mol. compn. of acid K sulfophosphates obtained at various P2O5/K2O ratios and temp. is presented.

CC 19-5 (Fertilizers, Soils, and Plant Nutrition)
Section cross-reference(s): 49

L51 ANSWER 9 OF 18 HCA COPYRIGHT 2004 ACS on STN

87:210147 Calculation of the deposition of a film of silicon dioxide and **phosphorus pentoxide** during the laminar **flow** of a gas mixture in a horizontal flat channel. Popov,

V. P.; Skoropanov, Yu. S. (USSR). Teplo- Massoobmen Dvukhfaznykh Sist. Fazovykh Khim. Prevrashch., 95-111. Editor(s): Ganzha, V. L.; Vinogradov, L. M.; Grushetskaya, S. M. Akad. Nauk BSSR, Inst. Teplo- Massoobmena: Minsk, USSR. (Russian) 1976. CODEN: 36LDAD.

AB A math. model was presented of P2O5 and SiO2 deposition during the oxidn. reaction of PH3 and SiH4 in the gas phase and in the reaction zone adjacent to the heated gas layer. Sep. particles of SiO2 and **P2O5 form** in that zone. At the oxidn. temp. 300-600°, the forming oxides are overcooled and susceptible to the formation of complexes. Therefore, the simultaneous formation of sep. oxide mols. and of complexes occurs. The diffusion coeffs. of the complexes are lower than the coeffs. of oxide particle diffusion. The results of the calcns. qual. agree with known exptl. data.

CC 76-13 (Electric Phenomena)
Section cross-reference(s): 78

L51 ANSWER 10 OF 18 HCA COPYRIGHT 2004 ACS on STN

83:193092 Azabicyclo derivatives. Kimura, Michio; Nakajima, Takeshi; Inaba, Shigeho; Yamamoto, Hisao (Sumitomo Chemical Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 50049297 19750501 Showa, 6 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1973-99969 19730904.

GI For diagram(s), see printed CA Issue.

AB Azabicyclo derivs. I (R1 to R5 = H, alkyl, OH, hydroxyalkyl, alkoxy, cyano, NH2, halo, CO2H, alkanoyl, aryl; R6 to R9 = H, alkyl) were prepd. by cyclization of tetrahydropyridines (II) or their salts with acids. Thus, 20 g 1-(3,3-dimethylallyl)-4-methyl-1,2,5,6-tetrahydropyridine was **stirred** with H3PO4-**P2O5** (**prepd.** from 270 g 85% H3PO4 and 214 g P2O5) 4 hr at 135-40° under N to give 4,4,6-trimethyl-1-azabicyclo[3.3.1]non-6-ene. I also prepd. were (R1 to R9 given): H, H, H, H, H, H, H, H, Me, Me; Me, Me, Me, H, H, H, H, Me, Me; H, Me, Me, H, H, H, H, Me, Me; and H, H, Me, H, H, H, H, Me, Et.

IC C07D; A61K

CC 27-17 (Heterocyclic Compounds (One Hetero Atom))

L51 ANSWER 11 OF 18 HCA COPYRIGHT 2004 ACS on STN

83:61882 Coating agents for polyolefin substrates. Miyakawa, Norio; Sato, Mitsuo; Kobayashi, Takashi (Mitsubishi Rayon Co., Ltd.). Jpn. Kokai Tokkyo Koho JP 49039623 19740413 Showa, 7 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1972-83657 19720823.

AB Polyolefin substrates are coated with a resin compn. comprising the reaction product of a hydroxy group-contg. polyester with one or more (meth)acrylic acids or their derivs., phosphates, prepd. by reaction of polyphosphoric acid or P2O5 with ethylenically-unsatd. hydroxy group-contg. monomer, and solvent, and irradiated, to give a coating film with good hardness and chem. resistance. Thus, 260 g of a polyester (prepd. from phthalic anhydride and ethylene

glycol) was heated 3 hr at 95° with acrylic acid 180, cyclohexane 60, p-toluenesulfonic acid 5, and hydroquinone 8 g to give a polyester polyacrylate in 80% yield. The reaction product of 2-hydroxyethyl methacrylate 520, hydroquinone 1, and **P205** 30 g was **stirred** with the polyester polyacrylate 520, Et acrylate 55, vinyltoluene 100, and TiO₂ 160 g to give a white enamel, which was coated (2 mm thickness) on a polypropylene molding piece, and irradiated with electron beams to give a coating film with pencil hardness H, and good chem. resistance and peel strength.

NCL 24H02; 24F0; 24C01

CC 42-2 (Coatings, Inks, and Related Products)

IT 2-Propenoic acid, 2-methyl-, 2-hydroxyethyl ester, reaction products with **phosphorus pentoxide** (polyester acrylate coatings contg., radiation-curable)

L51 ANSWER 12 OF 18 HCA COPYRIGHT 2004 ACS on STN

70:60839 Anticariogenic compositions. Muhler, Joseph C. (Indiana University Foundation). S. African ZA 6801030 19680710, 41 pp. (English). CODEN: SFXXAB. PRIORITY: US 19670307.

AB The title compns. were prepd. by the reaction of urea with P205 in an aq. environment in molar ratios of 2:1, 4:1, and 8:1. The compns. exhibited a high degree of anticariogenic effectiveness in the presence of sugar or in comestibles or in sugar-contg. comestibles. Thus, 30.0 g. chem. grade urea in 30 ml. redistd. H₂O in a 50-60° const. temp. bath treated within 5 min. with 71.0 g. **P205**, the mixt. **stirred** until viscous, maintained 48 hrs. at 50°, and dried 96 hrs. over CaCl₂ gave 99% product comprising mainly urea pyrophosphate (I). Similarly, the reaction of urea and P205 in a molar ratio of 4:1 as above gave mainly dimerized urea carbamido pyrophosphate (II), m. 110-16°, as well as minor amts. of urea carbamido pyrophosphate, diurea pyrophosphate, dimerized diurea pyrophosphate, urea orthophosphate, and carbamido phosphoric acid. Also similarly, the reaction of urea and P205 in a molar ratio of 8:1 as above gave mainly tetraurea pyrophosphate (III), m. 89.5-95.5°, as well as minor amts. of diurea dicarbamido pyrophosphate, diurea orthophosphate, and urea carbamido phosphate. II and III were characterized by x-ray diffraction methods; I is already known. Tests on rats measuring the redn. in enamel soly. indicated that the cariogenic potential of sugars and also of artificial sweeteners was reduced by incorporating at least 0.05% I, II, or III by wt. of the sugar, II and III being esp. effective. The LD₅₀ was detd. for II and III as 5.60 and 8.10 g./kg. resp., compared with 9.69 g./kg. for NaH₂PO₄.

CC 63 (Pharmaceuticals)

IT 1314-56-3

(reaction products with urea)

L51 ANSWER 13 OF 18 HCA COPYRIGHT 2004 ACS on STN

68:82416 Silicon elements for high-voltage rectifiers and for thyristors. (Associated Electrical Industries Ltd.). Fr. FR 1487219 19670630, 6 pp. (French). CODEN: FRXXAK. PRIORITY: GB 19650722.

AB Multilayer Si single-crystal semiconductor elements are prepd. by epitaxial deposition, covered with a layer of silicophosphate glass and heated in order to remove impurities (e.g. Cu by diffusion and absorption in this layer). A simple app. for this process comprises a silica-glass tube and a system of inlets and outlets making it possible to reverse the flow direction and to change the compn. of reaction gases without interrupting the process. The desired p or n layers are deposited on highpurity Si single-crystal plates resting on a quartz-covered graphite block and heated, preferably by induction. Doped layers result from a thermal decompn. of a mixt. of anhyd. H and suitable volatile compds. of Si and the doping element at 900-1300° (e.g., a good Si layer results at a growth rate of 2.5 μ /min. at 1250° and a flow rate of 1 l./min., from a mixt. of H with 2 mole % SiCl₄). After the epitaxial deposition has been completed, a silicophosphate glass layer is produced on the elements by **flowing P2O5** vapors through the tube (resulting from a mixt. of O and PH₃, or from passing a dry gas (O, N, Ar) over P2O5 heated to 200-800°) at 1000-1300°, or by application of a 2-methoxyethanol soln. of P2O5 and subsequent drying and heating to 1000-1300°. The elements are usually heated 1-3 hrs. Typical parameters are: temp. of P2O5 container 450°, Si element temp. 1200°, heating time 2 hrs., cooling rates 360°/hr. to 750° and 100-200°/min. from 750° to room temp. The diffusion of P into the element is much slower than that of the impurities into the glass layer; nevertheless a P-doped n-layer results on the surface, which can easily be removed chem. or mech., or preserved if an n-layer is needed on the surface. Multilayer elements are produced in this way for potentials of 2-5 kv. (depending on the thickness of the corresponding layer, which is 0.2-0.5 mm.) with a minority-carrier lifetime of 10-50 μ sec.

IC H01L; B01J

CC 71 (Electric Phenomena)

IT Electric rectifiers

(silicon controlled and high-voltage, epitaxy and gettering by phosphorus oxide (P2O5) in **manuf.** of)

L51 ANSWER 14 OF 18 HCA COPYRIGHT 2004 ACS on STN

60:21518 Original Reference No. 60:3756f-g Phosphoric acid anhydride. Klein, George I.; Newby, Ralph E.; Post, Leo B. (Stauffer Chemical Co.). US 3100693 19630813, 5 pp. (Unavailable). APPLICATION: US 19600617.

AB P2O5 is continuously condensed in a fluidized bed of P2O5 in an app.

providing an endless recirculating dry arm. Thus, P2O5, contg. 11-170 p.p.m. H2O vapor, produced in a combustion chamber, was introduced at 510-70° into the interior of a fluidized bed of granular P2O5 at 129° and with a d. of 40 lb./cu. ft. A free-flowing, dustless form of hexagonal P2O5 in the shape of small spheres or beads with a bulk d. of 67-74 lb./cu. ft. was produced at a rate of 5 lb./hr./cu. ft. of fluidized bed. The fluidizing gases were passed progressively in the closed system, (1) through a cyclone separator, which removed the larger particles of P2O5 and returned them to the bed, (2) through a scrubber using superphosphoric acid (77% P2O5 as the scrubbing medium) which removed the fines, and (3) a cooler, before being returned to the fluidized bed. As the P2O5 condensed on the P2O5 bed, the bed product was withdrawn continuously at the same rate.

NCL 023262000

CC 17 (Industrial Inorganic Chemicals)

L51 ANSWER 15 OF 18 HCA COPYRIGHT 2004 ACS on STN

56:24851 Original Reference No. 56:4654d-i,4655a-b Lignans. I.

Acylation in polyphosphoric acid as a route to intermediates.

Ayres, D. C.; Denney, R. C. (John Cass Coll., London). Journal of the Chemical Society, Abstracts 4506-9 (Unavailable) 1961. CODEN: JCSAAZ. ISSN: 0590-9791. OTHER SOURCES: CASREACT 56:24851.

AB Phenols and their ethers with alkoxybenzoic acids in polyphosphoric acid (PPA) gave esters and benzophenones, resp., the latter being intermediates in prospective syntheses of phenyltetrahydronaphthalene lignans. Phosphorylation was found to affect the course of some reactions. PPA was **prepd.** by mixing P2O5 8 with 90% H3PO4 (d. 1.75) 5 parts and stirring 30 min. at 85° before use. Vanillic acid (I) (5.0 g.) and 4.1 g. veratrole (II) stirred into PPA (from 50 g. P2O5) and the soln. kept 30 min. at 80-3° and poured into 250 ml. ice H2O gave 8.0 g. 4-hydroxy-3,3',4'-trimethoxybenzophenone (III), m. 142-3° (1:1 EtOH-H2O), ν 3300 and 1669 cm.-1 III (1.0 g.) in 3% aq. NaOH shaken 15 min. at room temp. with 1.0 g. Me2SO4 gave 0.81 g. [3,4-(MeO)2C6H3]2CO, m. 144° (EtOH), ν 1635 cm.-1 3,4,5-(MeO)3C6H2CO2H (IV) (4.6 g.) and 3.0 g. III in PPA (from 35 g. P2O5) treated as above gave 6.9 g. 3,4,5-(MeO)3C6H2COC6H3(OMe)2-3,4, m. 118-19° (EtOH), ν 1630 cm.-1 I (5 g.) and 3.2 g. PhOMe in PPA (from 50 g. P2O5) gave 8 g. 3,4-MeO(HO)C6H3COC6H4OMe-4 (V), m. 109-10°, ν 3300 and 1635 cm.-1 V (1.0 g.) methylated with 0.8 g. Me2SO4 as above and the mixt. heated 30 min. on a H2O bath gave 0.80 g. 3,4-(MeO)2C6H3COC6H4OMe-4, m. 98-9° (1:1 EtOH-H2O), ν 1636 cm.-1 IV (10.6 g.) and 8.4 g. 1,2,3-C6H3(OMe)3 (VI) in PPA (from 88 g. P2O5) treated as above gave 16.3 g. 2,3,4-(MeO)3C6H2COC6H2(OMe)3-3,4,5 (VII), m. 121° (aq. EtOH), ν 1650 cm.-1

1,2-CH₂O₂C₆H₄ (0.50 g.) in PPA stirred 2 hrs. at 20-2° and the mixt. dild. with H₂O gave 2 polymeric products, one (0.26 g.) by Et₂O extn. and the other (0.11 g.) by subsequent C₆H₆ extn. o-C₆H₄(OH)₂ (VIII) (13.0 g.) and 25.0 g. IV in PPA (from 200 g. P205) heated and **stirred** 40 min. at 85° and poured into 400 ml. ice H₂O gave 33 g. 2-HOC₆H₄O₂CC₆H₂(OMe)_{3-3,4,5} (IX), m. 178-9° (1:1 EtOH-H₂O), ν 3450 and 1736 cm.⁻¹ Repetition of this expt. with 11.0 g. VIII and 42.4 g. IV and the product (35 g.) washed with aq. NaHCO₃ gave 30 g. IX. VIII and 4,3,5-HO(MeO)₂C₆H₂CO₂H (X) (each 0.05 mole) treated as above gave 75% 4,3,5-HO(MeO)₂C₆H₂CO₂C₆H₄OH-2, m. 212° (1:1 EtOH-H₂O), ν 3350 and 1725 cm.⁻¹ 1,2-CPh₂O₂C₆H₃ (Mason, CA 39, 40642) (3.0 g.) and 2.32 g. IV in PPA (from 25 g. P205) treated as above (35 min. at 85°) gave 4.9 g. IX, m.p. and mixed m.p. 176-7° (4:1 EtOH-H₂O). VIII and IV (each 0.02 mole) refluxed 5 hrs. in 40 ml. Et₂O contg. 45% BF₃, the mixt. cooled, treated with 100 ml. H₂O, the Et₂O distd., the hot liquor decanted from 2 g. insol. oil, and the latter crystd. from 1:1 EtOH-H₂O gave IX, m. 179°; methylation of 1.0 g. IX gave 0.70 g. 2-MeOC₆H₄O₂CC₆H₂(OMe)_{3-3,4,5}, m. 113° (EtOH), an identical compd. being obtained on methylation of X prepd. above. VIII (2.5 g.) and 10.5 g. 3,4,5-(MeO)₃C₆H₂COC₆H₂ kept molten 2 hrs., the melt cooled, and the solid washed with aq. NaHCO₃ gave 11.4 g. o-C₆H₄[O₂CC₆H₂(OMe)_{3-3,4,5}]₂ (XI), m. 154° (1:1 C₆H₆-petr. ether). XI (4.0 g.) in 70 ml. PhNO₂ heated 4 hrs. on a steam bath with 3.5 g. AlCl₃ and the mixt. cooled, acidified with 20 ml. 5N HCl, and steam distd. gave 2.8 g. X, m. 203°; VIII was present in the steam distillate (FeCl₃ test). Gallic acid (XII) (4.0 g.) and 3.95 g. VI **stirred** in PPA (from P205), the soln. kept 1 hr. at 90°, poured into 100 ml. ice H₂O, the ppt. (0.5 g.) filtered off, the filtrate extd. with Et₂O (the ext. contained 2.2 g. material; the ppt. and the extd. material were a mixt. of XII and VI, predominantly VI), the aq. filtrate refluxed 2 hrs. with 200 ml. 2N HCl, and the product isolated with Et₂O gave 2.7 g. 3,4,5-(HO)₃C₆H₂COC₆H₂(OMe)_{3-2,3,4}, m. 181-2° (1:1 EtOH-H₂O), ν 3300 and 1663 cm.⁻¹, methylation giving 83% VII, m. 121-2°. 2-MeOC₆H₄OH (XIII) and I (each 0.03 mole) in PPA (from 50 g. P205) heated 30 min. at 80°, poured into 250 g. ice H₂O, and the mixt. worked up gave 74% recovered I and 60% recovered XIII; no ketone was detected.

CC 29 (Noncondensed Aromatic Compounds)

L51 ANSWER 16 OF 18 HCA COPYRIGHT 2004 ACS on STN

44:17709 Original Reference No. 44:3517h-i,3518a-b

Chloroalkanephosphonyl and -thiophosphonyl dichlorides. Woodstock, Willard H. (Victor Chemical Works). US 2495799 19500131 (Unavailable). APPLICATION: US .

AB Olefins with a terminal double bond and having only 1 alkyl group on

the 2-C atom add PCl_5 in the sense $-\text{C}(\text{PCl}_4)-\text{CCl}$; the **products** with P_2O_5 and P_2S_5 give, resp., 1-chloroalkane-2-phosphonyl or thiophosphonyl dichlorides. The products may be esterified, amidated, or hydrolyzed to the corresponding derivs. of the 1-chloroalkane-2-phosphonic or thiophosphonic acids. 1-Butene (125 g.) in 1200 ml. C_6H_6 treated at $0-5^\circ$ with 417 g. PCl_5 , stirred 6 hrs., treated with 106 g. P_2O_5 , stirred at room temp. 5 hrs., at 35° 4 hrs., and at 50° 9 hrs., filtered, concd. in vacuo, and distd. gave 224 g. $\text{EtCH}(\text{POCl}_2)\text{CH}_2\text{Cl}$, b18 $116-23^\circ$. Similarly, 81.5 g. 1-pentene in C_6H_6 with 208.5 g. PCl_5 , followed by 55 g. P_2O_5 (2 hrs. at room temp., 3 hrs. at 35° , and 3 hrs. at 50°), gave $\text{PrCH}(\text{POCl}_2)\text{CH}_2\text{Cl}$, b20 $130-2^\circ$, m. $39-42^\circ$, d25 1.319. Passage of 160 g. propene into 1200 ml. benzene contg. 208.5 g. PCl_5 for 11 hrs. at 20° , followed by 55 g. P_2O_5 and treatment as given above, resulted in $\text{MeCH}(\text{POCl}_2)\text{CH}_2\text{Cl}$, b. $190-218^\circ$. $\text{PrCH}(\text{POCl}_2)\text{CH}_2\text{Cl}$ (150 g.) and 200 g. BuOH stirred 25 min. at $25-30^\circ$, then 6 hrs. at 55° until HCl evolution stopped, gave $\text{PrCH}[\text{PO}(\text{OBu})_2]\text{CH}_2\text{Cl}$, b4 $154-62^\circ$, d25 1.106, m. below -70° . The esters are useful as oil-treating agents, flameproofing agents for textiles, and as fire-retarding plasticizers. Cf. C.A. 44, 7499e.

CC 10 (Organic Chemistry)

L51 ANSWER 17 OF 18 HCA COPYRIGHT 2004 ACS on STN

41:30993 Original Reference No. 41:6192c-g Intermolecular dehydrations by means of **phosphorus pentoxide**. I.

Preparation of substituted acetophenones. Kosolapoff, G. M. (Monsanto Chem. Co., Dayton, O.). Journal of the American Chemical Society, 69, 1651-2 (Unavailable) 1947. CODEN: JACSAT. ISSN: 0002-7863.

AB A no. of aromatic compds. have been condensed with AcOH to form the corresponding acetophenones, using about 0.5 mole P_2O_5 per mole AcOH . m- $\text{C}_6\text{H}_4\text{Me}_2$ (I) (106 g.) and 60 g. AcOH , treated with 3 g. celite and 71 g. P_2O_5 and stirred and refluxed 2 hrs., give 52 g. 2,4- $\text{Me}_2\text{C}_6\text{H}_3\text{Ac}_2$ (II), b20 $120-5^\circ$, and 10 g. 1,2,3,4- or 1,2,4,5- $\text{Me}_2\text{C}_6\text{H}_2\text{Ac}_2$ (III), b5 $100-5^\circ$; after heating 30 min., the yields were 53 g. II and 12 g. III; 53 g. I, 60 g. AcOH , and 71 g. P_2O_5 give after 2 hrs. 20 g. II, 30 g. III, and 20 g. residue. PhMe (92 g.), 60 g. AcOH , 71 g. P_2O_5 , and 3 g. celite, refluxed 2 hrs., give 15 g. p- $\text{MeC}_6\text{H}_4\text{Ac}$, b20 $115-20^\circ$. Cyclohexylbenzene similarly gives a small yield of cyclohexylacetophenone, b10 $150-60^\circ$. PhOMe (108 g.), 71 g. P_2O_5 , and 5 g. celite, treated at reflux temp. (30 min.) with 60 g. AcOH , give 30 g. PhOMe, 15 g. p- $\text{MeOC}_6\text{H}_4\text{Ac}$ (IV), 30 g. $\text{Ac}_2\text{C}_6\text{H}_3\text{OMe}$ (V), b30 $157-70^\circ$, and 70 g. residue; 324.4 g. PhOMe, 90 g. AcOH , 107 g. P_2O_5 , 200 cc. C_6H_6 , and 10 g. celite, refluxed 90 min., give 106.5 g. IV, 36.7 g. V, and 15.7 g. residue. PhOEt (122 g.), 60

g. AcOH, 71 g. P2O5, and 3 g. celite, refluxed 2 hrs., give 50 g. p-ETOC6H4Ac (VI) and 35 g. Ac2C6H3OEt (VII), b5 170-240°; 244 g. PhOEt, 60 g. AcOH, 71 g. P2O5, and 5 g. celite in 200 cc. C6H6, refluxed 75 min., give 152 g. PhOEt, 95 g. VI, and 20 g. VII; crystd. from EtOH, VII forms pale yellow plates, m. 141.5-2°. 1,3,5-C6H3Me3 (100 g.), 120 g. AcOH, 171 g. P2O5, and 5 g. celite, heated 90 min., give 82.5% 2,4,6-Me3C6H2Ac, b1 100-2°.

CC 10 (Organic Chemistry)

L51 ANSWER 18 OF 18 HCA COPYRIGHT 2004 ACS on STN

34:32171 Original Reference No. 34:4895c-f Treating hydrocarbon oils such as crude gasoline distillates with phosphorus pentoxide. Sachs, Albert P. (Petroleum Conversion Corp.). US 2191043 19400220 (Unavailable). APPLICATION: US .

AB An arrangement of app. is described, and a method for the treatment of low-boiling material such as a crude gasoline distillate with P2O5 to effect purification and utilize olefinic compds. present, which involves prepg. the material for treatment by removing therefrom substances sol. in dil. acid, then drying the hydrocarbons by contact therewith of P2O5 of not greater impurity than that which has been previously used in the main purifying treatment infra, and which is effective to remove potential water-forming compds. detrimental to the action of the relatively fresh P2O5 in the treatment infra, passing a liquid stream of the so pretreated hydrocarbon to the lower part of a previously formed column thereof, adding a suspension in hydrocarbon liquid of relatively fresh P2O5 to the upper part of the column, decanting from adjacent to the top of the column a stream of the hydrocarbon laden with **P2O5**, slowing up the **flow** of such stream sufficiently to cause added P2O5 to settle, recovering in **concd. form** the **P2O5** in suspension thus settled out, and recovering the treated hydrocarbons.

CC 22 (Petroleum, Lubricants, and Asphalt)

=> d his 152-

FILE 'HCA' ENTERED AT 15:44:05 ON 10 AUG 2004

L52 66291 S HEXAG?
 L53 269 S L4 AND L52
 L54 22 S L53 AND L5-L8
 L55 1 S L53 AND L9
 L56 0 S L53 AND (L28 OR L29)
 L57 20 S (L54 OR L55) NOT (L36 OR L51)

=> d 157 1-20 cbib abs hitind

L57 ANSWER 1 OF 20 HCA COPYRIGHT 2004 ACS on STN

125:180102 Infrared reflectance spectra and formalism of precipitation of acicular magnetic particles in network glasses. Ram, S.; Ram, K. (Institute of Metal Research, Technical University of Berlin, Berlin, D-10623, Germany). Infrared Physics & Technology, 37(4), 457-469 (English) 1996. CODEN: IPTEEY. ISSN: 1350-4495. Publisher: Elsevier.

AB 1-2 Mm thin platelets of borate or silicate glasses ppt. peculiarly isolated magnetic particles (of micrometer sizes) of **hexagonal** ferrites, spinel ferrites, or garnets at reaction temp. A small 0.5-3.0 mol % additive of Ag₂O, Bi₂O₃ or **P2O5** in these glasses behaves as a strong catalyst in undercooling the melt (in the shape of the platelets) in a truly amorphous metastable glass state of locally ordered network of interconnected basis structural units. In a typical 35BaO-25Fe₂O₃-40B₂O₃ borate glass, for example, the ordered structure in the 1-2 mm thin platelets results in 15-52 cm⁻¹ increase in the B-O stretching vibration frequencies over the usual values in the bulk. The surface tension σ (which is modified by the additives) of the glass-liq. facilitates the chem. ordering of planar configurations of interconnected (B₃O_{4.5})_n \rightarrow ∞ boroxol rings 1 over other along the surface of the platelets. On isothermal annealing at 500-850°, the planar network configurations (α) nucleate planar α - β interfaces with solid aggregates (β) of the immiscible (at this temp.) Ba²⁺ and Fe³⁺ cations caused in the network in the thermal induced recrystn. process of BaFe₁₂O₁₉ **hexagonal** ferrite. The initial shape and size of the α - β interface depends (in addn. to the σ and the free-energy difference ΔG_v between the 2 phases α and β) on the size and shape of the crystal (β) unit cell and the local structure of the glass. It therefore assumes an elongated shape in the elongated P6₃/mmc **hexagonal** crystal lattice (of crystallog. axial ratio c/a .apprx. 3.94) of BaFe₁₂O₁₉ ferrite. That ultimately grows and ppts. in BaFe₁₂O₁₉ single crystal in the presumed acicular shape (along the c-axis) over the network, following the **flow** of the heat released in the reaction along the planar interface, maintained by the strong surface tension σ , surface anisotropy (δ), and α - β wetting. The results are modeled and discussed using the B-O stretching or bending vibrations in the thin glass-platelets and the platelets milled (removing the rather long range at. ordering) into powder of particle size of 1 μ m or lower.

CC 73-3 (Optical, Electron, and Mass Spectroscopy and Other Related Properties)

Section cross-reference(s): 57, 77

IT 1304-76-3, Bismuth oxide (Bi₂O₃), uses **1314-56-3**, Phosphorus oxide (**P2O5**), uses 20667-12-3, Silver oxide (Ag₂O)

(IR reflectance spectra and formalism of pptn. of acicular magnetic particles in network glasses)

L57 ANSWER 2 OF 20 HCA COPYRIGHT 2004 ACS on STN

111:42331 Lithium-aluminum-phosphorus oxide molecular sieve compositions. Flanigen, Edith M.; Lesch, David A.; Lok, Brent M. T.; Patton, Robert L.; Wilson, Stephen T. (Union Carbide Corp., USA). U.S. US 4789535 A 19881206, 26 pp. Cont.-in-part of U.S. Ser. No. 599,811, abandoned. (English). CODEN: USXXAM. APPLICATION: US 1986-834921 19860228. PRIORITY: US 1984-599811 19840413.

AB The cryst. mol. sieves, having a 3-dimensional microporous framework structure of LiO_2 , AlO_2 , and PO_2 tetrahedral units and having the general (anhyd.) formula $mR:(\text{Li}_x\text{Al}_y\text{P}_z)\text{O}_2$ ($R = \geq 1$ org. templating agents present in the intercryst. pore system; m = molar amt. of R per mol $(\text{Li}_x\text{Al}_y\text{P}_z)\text{O}_2$ and has value 0 to .apprx.0.3; x, y, z = mol fraction of Li, Al, and P, resp.), are disclosed. The mol fractions are located within a (described) **hexagon** in a triangular Al-L-P diagram (d-spacings presented). The crystn. mechanism of these products is detd. by the addn. of ≥ 1 templating agents. To a mixt. of water 265.6 and hydrated Al oxide in the form of pseudo-boehmite phase comprising Al_2O_3 69.0 and H_2O 31.0 wt.% were added 40% Et4NOH 46.0 and Pr_3N 125.4 g, and the mixt. was **stirred** until homogeneous. To 100.9 g of this mixt. was added under stirring 0.6 g Li_3PO_4 . This mixt. was heated at 150° in a sealed and lined container for 16 h. The product contained C 4.9, N 0.66, Li_2O 0.71, Al_2O_3 34.4 and **P2O5** 44.7 wt.%, and had loss on ignition 20.4 wt.%, corresponding to the anhyd chem. compn. $0.04\text{Et}_4\text{NOH}:(\text{Li}_{0.04}\text{Al}_{0.50}\text{P}_{0.47})\text{O}_2$. X-ray diffraction data are presented.

IC ICM C01B025-26

NCL 423306000

CC 49-4 (Industrial Inorganic Chemicals)

L57 ANSWER 3 OF 20 HCA COPYRIGHT 2004 ACS on STN

86:109502 Refining of steelmaking slag. Ando, Ryo; Miyashita, Yoshio; Koyama, Tatsuo; Kubodera, Shoji (Nippon Kokan K. K., Japan). Jpn. Kokai Tokkyo Koho JP 51121422 19761023 Showa, 6 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1975-47328 19750418.

AB Molten slag in an elec. furnace having a **hexagonal** horizontal cross section is mixed with solid reductant and component-adjusting agent and **stirred** with an impeller to improve the slag reaction. By the method Fe, Mn, and P ore recycled and a cement clinker-like slag is obtained. For example, 10-ton converter slag contg. CaO 50.80, SiO_2 16.86, Al_2O_3 1.08, MgO and MnO 3.48 each, Fe 13.65, **P2O5** 2.20, and S 3.377% was treated with 0.6 ton powd. coke and 1 ton alumina in a furnace at 70 rpm with 300 kWh/ton to contain 56.40, 16.37, 11.14, 4.99,

0, 2.46, 0.30, and 0.25, resp., and to obtain 1.9-ton pig iron
[61933-23-1] contg. C 5.27, Si 0.28, Mn 12.70, P 2.75, and S 0.003%.

IC C21B003-06

CC 54-2 (Extractive Metallurgy)

L57 ANSWER 4 OF 20 HCA COPYRIGHT 2004 ACS on STN

59:25216 Original Reference No. 59:4563c-e Viscous **flow** and
melt allotropy of **phosphorus pentoxide**. Cormia,
R. L.; Mackenzie, J. D.; Turnbull, D. (Gen. Elec. Res. Lab.,
Schenectady, NY). Journal of Applied Physics, 34(8), 2245-8
(Unavailable) 1963. CODEN: JAPIAU. ISSN: 0021-8979.

AB The viscosity of liq. **P2O5** above and below the m.p. of the
tetragonal crystal was detd. by the falling-sphere method. At the
melting temp. of 580°, the viscosity is 5.15 + 106 P
and the activation energy for viscous **flow** is 41.5
kcal./mol. These values suggest that, similar to liq. B2O3, or
SiO2., the melt of tetragonal **P2O5** can be classified as a
network liq. From qual. observations on m. behavior and a
consideration of the ns of the cryst. and glassy phases,
hexagonal P2O5, on the other hand, gives a mol.
liq. on fusion. The "**hexagonal**" liq., however, is
unstable and undergoes rapid polymn. to give the network liq.

CC 3 (General Physical Chemistry)

IT Activation energy

(of **flow**, of **P2O5**)

IT Polymerization

(of phosphorus oxide (**P2O5**))

IT **Flow**

(of phosphorus oxide (**P2O5**) melts)

IT 1314-56-3, Phosphorus oxide, **P2O5**

(molten, allotropy and **flow** of)

L57 ANSWER 5 OF 20 HCA COPYRIGHT 2004 ACS on STN

57:3902 Original Reference No. 57:759e-i Heterocyclic compounds of
nitrogen. IV. A synthesis of 3-iodo-2-(o-iodophenyl)indole. Bruce,
J. Malcolm (Univ. Manchester, UK). Journal of the Chemical Society,
Abstracts 1514-15 (Unavailable) 1962. CODEN: JCSAAZ. ISSN:
0590-9791. OTHER SOURCES: CASREACT 57:3902.

AB cf. CA 54, 9883b. o-IC6H4COCl treated with diethyl
ethoxymagnesiummalonate and the mixt. hydrolyzed gave 84% o-ICr6H4Ac
(I), b0.05 85-6°; 2,4-dinitrophenylhydrazone, orange
hexagonal plates, m. 187.5° (BuOH); semicarbazone,
hexagonal plates, m. 181-1.5° (EtOH). I (1.28 g.),
0.54 g. PhNHNH2, 1.5 g. 88-90% H3PO4, and 1 g. **P2O5** were
stirred at 110°, the reaction allowed to subside, and
the temp. raised to 150°, when an exothermic reaction
occurred; the mixt. heated 2 min. at 180°, cooled, dild. with
12 ml. water, extd. with ether, washed, dried, the solvent removed,

and the residue distd. gave 0.12 g. I and 27% 2-(0iodophenyl)indole (II), orange-yellow viscous oil; 1,3,5trinitrobenzene adduct, deep red needles, m. 115.5-16° (C6H6-ligroine). Alternately, 4.82 g. I and 2.16 g. PhNH-NH2 were heated 30 min. at 150°, then 30 min. at 100°/30 mm.; 30 g. powd. anhyd. ZnCl2 was added, the mixt. **stirred** 15 min. at 180°, cooled, and digested on a water bath with 50 ml. 2% HCl until no further material dissolved; extn. with C6H6 was followed by washing with HCl, water, and drying; the soln. was concd. to 25 ml., chromatographed on Al2O3, duted with C6H6 until it was no longer yellow, and the solvent removed and distd. to give 57% II. II (3.61 g.) in 15 ml. C5H5N at 0° was treated 115 min. with 1.98 g. ICl in 15 ml. dioxane, and kept 60 hrs. at 0° the solvent was removed at 25 mm., the residue dild. with water, extd. with ether, washed with water, dried, and evapd.; the residue in 10 ml. C6H6 was chromatographed on Al2O3 and eluted with C6H6 until colorless. Removal of solvent and crystn. from 30 ml. cyclohexane gave 76% 3-iodo-2-(0iodophenyl)indole (III), m. 124.5-5°; 1,3,5-trinitrobenzene adduct, orange-red laths, m. 141° (C6H6-tigroine). III heated with Cu2O gave II; III similarly heated with Cu2O, prepd. by redn. of Cu(OAc)2 with N2H4, gave 2-phenylindole, m. 189.5-90°.

CC 31 (Heterocyclic Compounds-One Hetero Atom)

L57 ANSWER 6 OF 20 HCA COPYRIGHT 2004 ACS on STN

54:118062 Original Reference No. 54:22507e-i,22508a-i,22509a-i,22510a-g
Elimination of nonangular alkyl groups in aromatization reactions.
IV. Cocker, Wesley; Hopkins, L. O.; Mabrouk, L.; McCormick, J.;
McMurry, T. B. H. (Trinity Coll., Dublin, Ire.). Journal of the
Chemical Society, Abstracts 2230-42 (Unavailable) 1960. CODEN:
JCSAAZ. ISSN: 0590-9791.

AB cf. CA 49, 8891e. New di-, tri-, and tetraalkylnaphthalenes were synthesized, including 2 completely substituted in the peri positions. Their infrared spectra were recorded. Spectroscopic characteristics of the last 2 compds. showed no abnormalities which could arise from overlap of the alkyl groups. Two cases of the loss of Et group during dehydrogenation with Se and with Pd-C were reported. β -Benzoyl- α -methylpropionic acid (38 g.) with CH2N2 in MeOH-Et2O gave 37 g. Me β -benzoyl- α -methylpropionate (I), prisms, m. 56°. EtMgI (from 39 g. EtI, 6 g. Mg, and 86 cc. Et2O) added slowly to 5 g. I in 20 cc. Et2O, the mixt. refluxed 1 hr., set aside overnight, and the complex decompd. gave 0.5 g. Me 2-methyl-4-phenyl-3-hexenoate (II), b17 165°, n20D 1.5194, λ 243.5 m μ , log ϵ 3.24, ν 1770 cm.-1 I (20.6 g.) in 100 cc. Et2O added dropwise to 0.138 mole EtMgI in 50 cc. Et2O at 0°, after 0.5 hr. the mixt. allowed to warm to room temp., 30 cc. PhMe added, the Et2O removed, the residue heated 6 hrs. at 100°, and worked up as usual gave 16 g. II;

S-benzylisothiuronium salt m. 126°. II (15 g.) in 60 cc. MeOH with 1 g. Raney Ni at 100°/70 atm. H gave 12.4 g. 2-methyl-4-phenylhexanoic acid (III), b17 183°, ν 1706 cm.-1 III (12.4 g.) added to cold polyphosphoric acid (from 33.4 cc. 90% H3PO4 and 35.3 g. P2O5) in 1 hr. at 165°, the mixt. heated 5 min. at 165°, cooled, poured into cold H2O, and extd. with Et2O gave 8.5 g. 4-ethyl-1,2,3,4-tetrahydro-2-methyl-1-oxonaphthalene (IV), b1 101°, ν 1691 cm.-1 IV (3 g.), 60 cc. PhMe, 5 cc. AcOH, 200 cc. HCl, 45 cc. H2O, and 80 g. Zn-Hg refluxed 60 hrs. gave 1 g. 4-ethyl-1,2,3,4-tetrahydro-2-methylnaphthalene (V), b1 71°. V (0.9 g.) heated 4 hrs. at 260-80° with 0.9 g. Pd-C, the product collected in Et2O, and distd. gave 0.2 g. 1-ethyl-3-methylnaphthalene, b22 140°, n24D 1.5969; picrate, brick-red needles, m. 112.5° (MeOH); trinitrobenzene adduct m. 115° (MeOH); styphnate, yellow needles, m. 119.5° (AcOH); trinitrotoluene adduct m. 75° (MeOH). α -Bromopropiophenone (45.5 g.) heated 6 hrs. with 6 g. Na and 45.5 g. Et malonate in 200 cc. C6H6 and the ester hydrolyzed with excess MeOH-KOH gave 15 g. 1-benzoyl-ethylmalonic acid (VI), m. 158°. VI heated at 160° until effervescence ceased gave 5.5 g. β -benzoylbutyric acid (VII), prisms, m. 58° (H2O). VII (5.5 g.) refluxed 40 hrs. with 20 cc. concd. HCl, 9 cc. H2O, 12 cc. PhMe, and 16 g. Zn-Hg gave 3.5 g. β -methyl- γ -phenylbutyric acid (VIII), b15 172°, ν 1716, 1794 cm.-1 VIII (2.4 g.) heated 10 min. at 90° with 16 cc. concd. H2SO4, poured on H2O, and extd. with Et2O gave 1 g. 1,2,3,4-tetrahydro-3-methyl-1-oxonaphthalene (IX), b14 128°. IX (0.9 g.) in 20 cc. Et2O refluxed 3 hrs. with EtMgI (from 5 cc. EtI) and the complex decompd. gave 0.6 g. 1-ethyl-3,4-dihydro-3-methylnaphthalene, b14 136°. EtHC(CO2Et)2 (188 g.) added slowly to NaOEt (from 23 g. Na), the mixt. cooled, 1 g. NaI added followed by dropwise addn. of 122.5 g. ClCH2CO2Et, the mixt. refluxed 20 hrs., the alc. removed, the residue dild. with H2O, and extd. with Et2O gave 150 g. tri-Et butane-1,2,2-tricarboxylate (X), b60 193°. X refluxed with excess concd. HCl gave 60 g. ethylsuccinic acid (XI), m. 97° (C6H6-Et2O). XI (60 g.) distd. and then redistd. gave 45 g. ethylsuccinic anhydride (XII), b25 146°. AlCl3 (180 g.) added to 74 g. XII in 65 cc. C6H6 and 225 cc. CH2Cl2 and the mixt. **stirred** 18 hrs. gave 78 g. β -benzoyl- α -ethylpropionic acid, m. 85° (ligroine); Me ester (XIII) b1 132°, ν 1730 and 1685 cm.-1. BzH (1.06 g.) in 15 cc. MeOH heated 10 min. at 40° with 1 g. XIII and 0.54 g. NaOMe in 5 cc. MeOH, the mixt. set aside overnight, the MeOH removed, the residue acidified, and extd. with Et2O gave 1.5 g. 3-benzoyl-2-ethyl-4-phenyl-3-butenic acid, m. 123° (ligroine), ν 1702, 1651, 1600 cm.-1 XIII (30 g.) and MeMgI (from 27.43 g. MeI) gave 19 g. 2-ethyl-4-phenylpent-3-enoic acid (XIV), b1

135°, m. 50-1°, ν 1700 cm.⁻¹ XIV (32 g.)
hydrogenated over Raney Ni in MeOH at 100°/80 atm. gave Me
ester, hydrolyzed with 7.5% MeOH-KOH to 17 g. α -ethyl- γ -
phenylvaleric acid (XV), b1 139°, ν 1700 cm.⁻¹
Cyclization of 17 g. XV with polyphosphoric acid gave 9 g.
2-ethyl-1,2,3,4-tetrahydro-4-methyl-1-oxonaphthalene (XVI), b1
123°, λ 248 and 289 m μ , log ϵ 4.98 and
4.16, ν 1680 cm.⁻¹ XVI (3 g.) reduced as above gave 1 g.
3-ethyl-1,2,3,4-tetrahydro-1-methylnaphthalene (XVII), b1
77°. XVII (0.6 g.) heated 4.5 hrs. at 260-70° with
0.6 g. Pd-C and the product extd. with C₆H₆ gave
3-ethyl-1-methylnaphthalene, oil; picrate, orange needles, m.
83° (MeOH). β -(p-Ethylbenzoyl)propionic acid (30 g.)
refluxed 2 hrs. with 50 cc. MeOH and 5 cc. concd. H₂SO₄ gave 28.8 g.
Me ester (XVIII), b1 134°, m. 33°, ν 1754 cm.⁻¹
EtMgI (from 30.2 g. EtI) in 60 cc. Et₂O treated with 28.8 g. XVIII
in 100 cc. Et₂O gave 12.5 g. 4-(p-ethylphenyl)-3-hexenoic acid
(XIX), oil, b1 182°, ν 1715 cm.⁻¹ XIX (12.5 g.) in 100
cc. MeOH hydrogenated over Raney Ni at 100°/110 atm. gave a
mixture of satd. acid and ester, which refluxed 2 hrs. with 50 cc. 5%
MeOH-KOH gave 5.5 g. 4-(p-ethylphenyl)hexanoic acid (XX), b1
132-3°, ν 1700 cm.⁻¹ XX (12 g.) cyclized with
polyphosphoric acid 3 min. at 165° gave 9 g.
1,6-diethyl-1,2,3,4-tetrahydro-4-oxonaphthalene (XXI), b1
117-18°, ν 1680 cm.⁻¹ XXI (3.3 g.) in 60 cc. PhMe
refluxed 42 hrs. at 260-80° with 80 g. Zn-Hg, 100 cc. concd.
HCl, and 5 cc. AcOH in 45 cc. H₂O gave 1.2 g. 1,6-diethyl-1,2,3,4-
tetrahydronaphthalene (XXII), b1 92°. XXII (1 g.) heated 4
hrs. at 260-80° with 1 g. Pd-C gave 0.8 g.
1,6-diethylnaphthalene, b1 76°, n_D 1.5806; picrate m.
70° (MeOH). 7-Ethyl-1,2,3,4-tetrahydro-1-oxonaphthalene (7.7
g.) in 25 cc. Et₂O refluxed 3 hrs. with EtMgI (from 12.3 g. EtI),
the product set aside 2 hrs. with 20 cc. anhyd. HCO₂H, poured into
H₂O, and extd. with Et₂O gave 5.7 g. 1,7-diethyl-3,4-
dihydronaphthalene (XXIII), b1 79°. Dehydrogenation of 3 g.
XXIII with Pd-C 4 hrs. at 260-70° gave 2.5 g.
1,7-diethylnaphthalene, b1 87°, n_D 1.5858; picrate, orange
needles, m. 78°. XVI (1 g.) in 10 cc. Et₂O refluxed 7 hrs.
with MeMgI (from 3.5 g. MeI), left overnight, and the complex
decompd. gave 0.6 g. 3-ethyl-1,2-dihydro-1,4-dimethylnaphthalene
(XXIV), b1 75°. XXIV (0.4 g.) heated 4.5 hrs. at
260-80° with Pd-C gave 2-ethyl-1,4-dimethylnaphthalene, oil;
trinitrobenzene adduct, yellow needles, m. 123° (MeOH). IV
(2.5 g.) in 10 cc. Et₂O refluxed 2 hrs. with MeMgI (from 3.8 g. MeI)
and decompd. with ice and NH₄Cl gave 4-ethyl-1,2,3,4-tetrahydro-1-
hydroxy-1,2-dimethylnaphthalene (XXV), **hexagonal** prisms,
m. 73° (ligroine). XXV set aside 2 hrs. with 10 cc. anhyd.
HCO₂H gave 1-ethyl-1,2-dihydro-3,4-dimethylnaphthalene (XXVI), b1

150°. XXVI (1.3 g.) heated 4 hrs. at 260-80° with 1.3 g. Pd-C and the product extd. with MeOH gave 0.8 g. 4-ethyl-1,2-dimethylnaphthalene, b1 136°, n_D 1.6021; picrate, orange needles, m. 117° (MeOH); trinitrobenzene adduct, golden needles, m. 118° (MeOH); styphnate, orange needles, m. 119° (AcOH). I (14 g.) in 75 cc. Et₂O refluxed 3 hrs. with MeMgI (from 13.3 g. MeI), set aside 18 hrs., the complex decompd., the mixt. extd. with Et₂O, and the ext. washed with 5% Na₂CO₃ gave 3 g. 2-methyl-4-phenyl-3-pentenoic acid (XXVII), b1 150°, ν 1712 cm.⁻¹ The ether ext. afforded 6.5 g. neutral oil, b1 118°, ν 1778 cm.⁻¹ Hydrolysis of the oil 3 hrs. with 36 cc. 5% MeOH-KOH gave 5 g. XXVII. XXVII (12 g.) in 50 cc. MeOH hydrogenated over Raney Ni at 10°/70 atm. gave the satd. ester. Hydrolysis of the ester 2 hrs. with 100 cc. 5% MeOH-KOH gave 10 g. α -methyl- γ -phenylvaleric acid (XXVIII), b1 125°, ν 1713 cm.⁻¹ XXVIII (4.8 g.) heated 3 min. at 165° with polyphosphoric acid gave 2.6 g. 1,2,3,4-tetrahydro-2,4-dimethyl-1-oxonaphthalene (XXIX), b1 88-9°, ν 1694 cm.⁻¹ XXIX (1.4 g.) in 10 cc. Et₂O refluxed 3 hrs. with EtMgI (from 3.8 g. EtI), the complex decompd., and extd. with Et₂O gave 0.9 g. 4-ethyl-1,2-dihydro-4-hydroxy-1,3-dimethylnaphthalene (XXX), **hexagonal** prisms, m. 85° (ligroine). XXX set aside 2 hrs. with 10 cc. anhyd. HCO₂H gave 0.7 g. 4-ethyl-1,2-dihydro-1,3-dimethylnaphthalene (XXXI), b1 95°. XXXI (0.6 g.) heated 3 hrs. at 260-80° with 0.6 g. Pd-C and the mixt. extd. with C₆H₆ gave 1 g. 1-ethyl-2,4-dimethylnaphthalene, b2 109°, n_D 1.5975; picrate m. 94° (MeOH). Me β -(p-toluoyl)propionate (41 g.) in 100 ml. Et₂O treated with EtMgI (from 43 g. EtI) gave 15 g. 4-(p-tolyl)-3-hexenoic acid (XXXII), b1 137-41°, ν 1710 cm.⁻¹ XXXII (20 g.) hydrogenated in 75 cc. MeOH over 2 g. Raney Ni at 100°/80 atm. gave 20 g. Me 4-(p-tolyl)hexanoate (XXXIII), b1 99°, ν 1740 cm.⁻¹ Hydrolysis of XXXIII with 120 cc. 5% MeOH-KOH gave 17 g. 4-(p-tolyl)hexanoic acid (XXXIV), b1 155°, m. 36°. XXXIV (16 g.) heated 5 min. at 165° with polyphosphoric acid and the mixt. extd. with Et₂O gave 15 g. 4-ethyl-1,2,3,4-tetrahydro-7-methyl-1-oxonaphthalene (XXXV), b2 134°, λ 254 and 295 m μ , log ϵ 4.21 and 3.74, ν 1683 cm.⁻¹; semicarbazone, rhombs, m. 165-6° (dil. alc.). XXXV (5 g.) in 25 cc. Et₂O refluxed 3.5 hrs. with MeMgI soln. gave 3 g. 1-ethyl-1,2-dihydro-4,6-dimethylnaphthalene (XXXVI), b1 115°. XXXVI (2 g.) heated 4 hrs. at 260-80° with 2 g. Pd-C and the product extd. with C₆H₆ gave 1.3 g. 1-ethyl-4,6-dimethylnaphthalene, b1 85°; picrate, orange needles, m. 85° (MeOH); trinitrobenzene adduct, yellow needles, m. 109° (MeOH). IV (2.9 g.) in 15 cc. Et₂O refluxed 4 hrs. with EtMgI soln. and the product set aside 2 hrs. in 10 cc. anhyd. HCO₂H, dild. with H₂O, and extd. with Et₂O

gave 1.5 g. 1,4-diethyl-1,2-dihydro-3-methylnaphthalene (XXXVII), b1 140°. XXXVII (9.4 g.) heated 4 hrs. with 1.4 g. Pd-C at 260-80° gave 0.8 g. 1,4-diethyl-2-methylnaphthalene, b1 142°, n21D 1.5935; picrate, orange-red needles, m. 62° (MeOH); trinitrobenzene adduct m. 97° (MeOH); trinitrotoluene adduct, yellow needles, m. 68° (MeOH). XXXV (5 g.) in 25 cc. Et2O refluxed 4 hrs. with EtMgI soln. gave 2.7 g. dihydro compd., b2 123°. The dihydro compd. (2 g.) heated 4 hrs. at 260-80° with 2 g. Pd-C gave 1.2 g. 1,4-diethyl-6-methylnaphthalene, b1 112°; picrate m. 71-2° (MeOH); trinitrobenzene adduct m. 101°. XXI (3.3 g.) in 10 cc. Et2O refluxed 2 hrs. with MeMgI (from 2 cc. MeI) and set aside 2 hrs. with 12 cc. HCO2H gave 3 g. 1,6-diethyl-1,2-dihydro-4-methylnaphthalene (XXXVIII), b1 89°. XXXVIII (1.4 g.) heated 4 hrs. at 260-80° with 1.4 g. Pd-C gave 1.1 g. 1,6-diethyl-4-methylnaphthalene, b1 90°, n21D 1.5859; picrate m. 56°; trinitrobenzene adduct m. 80° (MeOH). XVIII (84.4 g.) in 250 cc. Et2O refluxed 5 hrs. with MeMgI (from 75.2 g. MeI) gave 6.5 g. 4-(p-ethylphenyl)-3-pentenoic acid (XXXIX), b1 138°, ν 1719 cm.-1. Crude XXXIX (10 g.) hydrogenated 6 hrs. in 50 cc. MeOH over 1 g. Raney Ni at 100°/110 atm. and hydrolyzed with 100 cc. 5% MeOH-KOH gave 9.5 g. γ -(p-ethylphenyl)valeric acid (XL), b1 137°, ν 1706 cm.-1. XL (6 g.) cyclized with polyphosphoric acid gave 4.5 g. 6-ethyl-1,2,3,4-tetrahydro-1-methyl-4-oxonaphthalene (XLI), b1 113°, ν 1682 cm.-1. XLI (2.5 g.) in 15 cc. Et2O refluxed 4 hrs. with EtMgI (from 6.7 g. EtI) and the product set aside 2 hrs. in 10 cc. anhyd. HCO2H gave 1.6 g. 4,6-diethyl-1,2-dihydro-1-methylnaphthalene (XLII), b1 96°. XLII (1.2 g.) heated 4 hrs. at 260-70° with 1.2 g. Pd-C gave 0.9 g. 4,6-diethyl-1-methylnaphthalene, b. 110°, n25D 1.5808; picrate m. 76.5°. XXI (4 g.) in 12 cc. Et2O refluxed 2 hrs. with EtMgI and the product set aside 2 hrs. in 10 cc. anhyd. HCO2H gave 3.1 g. 1,4,6-triethyl-1,2-dihydronaphthalene (XLIII), b1 119°. XLIII (2.9 g.) heated 4 hrs. at 260-80° with 2.9 g. Pd-C gave 2 g. 1,4,6-triethylnaphthalene, b3 128°, n25D 1.5770; picrate m. 53°. Me β -(2,5-dimethylbenzoyl)propionate (XLIV) (21 g.) was obtained as an oil, b1 148°, n19D 1.5202, ν 1754 cm.-1, when the corresponding acid (30 g.) was refluxed 2 hrs. with MeOH-H2SO4. XLIV (15 g.) in 20 cc. Et2O treated 18 hrs. with EtMgI gave 5 g. 4-(2,5-dimethylphenyl)hex-3-enoic acid (XLV), b1 146°, ν 1715 cm.-1, along with recovered XLIV. XLV (30 g.) hydrogenated in 80 cc. MeOH over 2 g. Raney Ni at 100°/120 atm. gave 32 g. Me 4-(2,5-dimethylphenyl)hexanoate (XLVI), b1 133°, 1745 cm.-1; XLVI refluxed 6 hrs. with 160 cc. 5% MeOH-KOH gave 22.5 g. 4-(2,5-dimethylphenyl)hexanoic acid (XLVII), b1 149°, 1715 cm.-1. XLVII (12.4 g.) heated 5 min. at 165° with

polyphosphoric acid gave 7.8 g. 1-ethyl-1,2,3,4-tetrahydro-5,8-dimethyl-4-oxonaphthalene (XLVIII), b1 121°, ν 1675 cm.⁻¹ XLVIII (3 g.) in 15 cc. Et2O refluxed 14 hrs. with MeMgI (from 4.2 g. MeI) gave 0.4 g. 1-ethyl-1,2-dihydro-4,5,8-trimethylnaphthalene (XLIX), b1 120°. XLIX (0.4 g.) heated 3 hrs. with 0.4 g. Pd-C gave 0.2 g. 1-ethyl-4,5,8-trimethylnaphthalene, b3 118°, n19D 1.5841; picrate, brick-red needles, m. 110° (MeOH). XLVIII (5 g.) in 25 cc. Et2O with EtMgI gave a product which set aside 2 hrs. in 20 cc. HCO2H gave 1.7 g. 1,4-diethyl-1,2-dihydro-5,8-dimethylnaphthalene (L), b1 101°. L (1.3 g.) heated 4 hrs. at 260-80° with 1.3 g. Pd-C gave 1 g. 1,4-diethyl-5,8-dimethylnaphthalene, b1 107°, n20D 1.5844; picrate m. 135° (MeOH). β -(o-Methoxyphenyl)butyric acid (25 g.) refluxed 1 hr. with 20 cc. SOCl2 gave 24.7 g. β -(o-methoxyphenyl)butyryl chloride (LI), b3 144-5°. LI (26.1 g.) in 150 cc. Et2O slowly added to 12.1 g. CH2N2 in 700 cc. Et2O, the mixt. set aside 2 days, the solvent removed, the residue dissolved in 257 cc. dioxane at 50°, heated 2 hrs. with a mixt. of 150 cc. 30% NH4OH and 40 cc. 10% AgNO3, filtered, the solvents evapd., and the residue triturated with ligroine gave 16.2 g. γ -(o-methoxyphenyl)valeramide (LII), m. 76° (C6H6). LII (16.2 g.) refluxed 5 hrs. with 100 cc. 15% aq. KOH, the mixt. acidified, and extd. with Et2O gave 16 g. γ -(o-methoxyphenyl)valeric acid (LIII), prisms, m. 66-7° (ligroine). LIII (15 g.) heated 5 min. at 165° with polyphosphoric acid, cooled, poured on ice, extd. with Et2O, and evapd. gave 4.1 g. solid, C12H14O2, m. 242° (EtOAc). The oil from the filtrate distd. gave 5.5 g. 1,2,3,4-tetrahydro-5-methoxy-4-methyl-1-oxonaphthalene (LIV), b1 107°, ν 1686 cm.⁻¹ LIV (5.5 g.) reduced 30 hrs. with 69 g. Zn-Hg in 69 cc. concd. HCl, 42 cc. H2O, 1.5 cc. AcOH, and 20 cc. PhMe gave 3.3 g. 1,2,3,4-tetrahydro-5-methoxy-4-methylnaphthalene (LV), b. 78°. LV (3.4 g.) heated 4 hrs. at 260-80° with 3.4 g. Pd-C gave 2.1 g. 1-methylnaphthalene, b1 60° (picrate m. 143°), and 0.1 g. 1-methoxy-8-methylnaphthalene (LVI), b1 98° (picrate m. 154°). LV (2.2 g.) heated 3 hrs. with 0.4 g. S at 220-30° gave 1.2 g. LVI, n26D 1.5625, λ 229, 280, 292, and 326 m μ , log ϵ 4.48, 3.54, 3.55, and 2.98. LVI refluxed 2 hrs. with 30 cc. HI and 33 cc. AcOH, cooled, dild., extd. with Et2O, the ext. washed and treated with 10% NaOH, the alk. ext. acidified, and extd. with Et2O gave 0.3 g. naphthol, b4 110°; picrate m. 190° (MeOH).

CC 10F (Organic Chemistry: Condensed Carbocyclic Compounds)

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52:40407 Original Reference No. 52:7214c-i,7215a-f Natural tannins. XXVIII. Synthesis of 1,3,6-trigalloylglucose. Schmidt, Otto Th.; Klinger, Gunther (Univ. Heidelberg, Germany). Ann., 609, 199-208

(Unavailable) 1957.

AB All evapns. were carried out in vacuo. Soly. data for all new compds. are given. Unless otherwise stated, compds. were dried over **P2O5** at 40-80°/0.3-2 mm. Triacetyllevoglucosan (15 g.) was benzylated by Zemplen's method (cf. Z., et al., C.A. 31, 85141); the crude product in 50 cc. Pr2O was dried with Na2SO4 and filtered, giving 20% 2,4-dibenzyllevoglucosan (I), needles or leaflets, m. 106.5-107° (EtOH), $[\alpha]_{20D} -28.5^\circ$ (c 3.4, CHCl3). 2,4-Dibenzylglucose (II) (prepd. by Z.'s method, loc. cit.), recrystd. from aq. dioxane, Me2CO, or EtOH and air-dried formed II.0.5H2O, m. 100-3° (by preheating the block to 95°), $[\alpha]_{20D} 32.4 \pm 0.5^\circ$ (c 5, EtOH). (Z. gives 75-9°, and $[\alpha]_{20D} 25.1^\circ$). Under carefully controlled, fully described conditions anhyd. cryst. II, m. 117-20°, $[\alpha]_{20D} 35 \pm 0.8^\circ$ (c 3.5, EtOH), was obtained. Neither form of II shows mutarotation. Anhyd. II (1.5 g.) and 9 g. tribenzylgalloyl chloride (IIa) in 50 cc. purified dry CHCl3 and 2.5 cc. quinoline, kept 2 days at 40°, and 6 days at 60°, dild. with 200 cc. CHCl3 and washed successively with 2N H2SO4, dil. NaHCO3 and H2O, dried, evapd., dissolved in 40 cc. C6H6, kept 24 hrs. with sepn. of 2.4 g. tribenzylgallic acid (III). The C6H6 mother liquor was chromatographed on Woelm neutral Al2O3 (IIIa), eluted with C6H6; the sirup from the evapd. eluate in 15 cc. AcOEt at 0° gave 2.1 g. tribenzylgallic anhydride (IV), m. 166°, the evapd. mother liquor from which yielded small amts. of IV and 0.1 g. 1,6(?) -bis(tribenzylgalloyl)-2,4-dibenzylglucose (V), m. 104° (AcOMe), $[\alpha]_{20D} 28^\circ$ (c 2, AcOEt). To 34.88 g. III in dry dioxane and 13.84 g. AgNO3 in 100 cc. H2O and 150 cc. MeOH were added 23 cc. 6% NH3 in MeOH, giving, after 24 hrs. at 0°, 34 g. Ag salt (VI) of III, decomp. 245°, difficultly sol. or insol. in neutral solvents, sol. in dioxane contg. acid or NH3; quite stable to light, but not direct sunlight. Acetobromoglucose (2.55 g.) and 3.42 g. powd. VI, suspended and shaken in 70 cc. PhMe was refluxed 4 min., cooled, filtered, and passed through IIIa which was then washed with 50 cc. C6H6. The filtrate and washings, evapd. gave 3.2 g. 1-(tribenzylgalloyl)-2,3,4,6-tetraacetyl- β -D-glucose, m. 150° (BuOH), $[\alpha]_{20D} -24.7^\circ$ (c 4, AcOEt), 2.13 g. of which, hydrogenated in 20 cc. abs. MeOH and 40 cc. AcOEt, with 0.06 g. Pd gave 1-galloyl-2,3,4,6-tetraacetyl- β -D-glucose (VII), cubes or thick needles, m. 200° (aq. MeOH), $[\alpha]_{20D} -47^\circ$ (c 2, MeOH), which was deacetylated at 20° with MeONa in abs. EtOH, giving glucogallin, m. 216-18°. VIII with Ac2O and pyridine gave heptaacetylglucogallin, m. 125-6°, $[\alpha]_{20D} -24^\circ$ [(CHCl2)2]. I (10.3 g.) and 16.5 g. IIa in 50 cc. pyridine kept 8 days at 40°, poured into 0.5 l. H2O and **stirred** intermittently during 24 hrs., gave a ppt. which, after washing with H2O was dried over H2SO4. This mixt. in 180 cc.

warm C₆H₆ was kept 24 hrs. at 20° and filtered, and the filtrate dild. with 180 cc. C₆H₆, passed through IIIa, evapd. to dryness, and dissolved in boiling iso-Pr₂O giving 17.6 g. (crude) 3-(tribenzylgalloyl)deriv. (VIII) of I, C₄₈H₄₄O₉, m. 90° (MeOH or iso-Pr₂O), [α]₂₀D -31° (c 2, AcOEt). VIII (3.05 g.) in 30 cc. AcOEt and 20 cc. MeOH, hydrogenated with 0.06 h. Pd gave 3-galloyllevoglucosan, **hexagons**, m. 250° (without decompn.) (H₂O), [α]₂₀D -49.5° (c 2, abs. MeOH); pentaacetate, m. 150° (MeOH), [α]₂₀D -34.2° (c 2, CHCl₃). To VIII (4 g.) in 91 cc. C₆H₆ was added 16.8 gg. (CF₃CO)₂O followed by the dropwise addn. of 2.8 cc. of a soln. (VIIIa) prepd. at 0° by adding 1 cc. H₂SO₄ to 10 cc. anhyd. dioxane. The mixt. kept sealed 24 hrs. at 20°, was poured into ice-H₂O and extd. with a mixt. of 120 cc. AcOEt and 200 cc. Et₂O; the org. phase washed 8 times with 90 cc. each of a satd. NaHCO₃ soln. and twice with satd. Na₂SO₄, dried over Na₂SO₄, decolorized with little C, evapd. to dryness, refluxed 1-1.5 hrs. with MeOH, evapd., dried over P₂O₅, taken up in 100 cc. AcOEt, and chromatographed on IIIa, yielded unchanged VIII in the 1st 300 cc. (AcOEt) eluate. The following 200 cc. AcOEt combined with a succeeding 250 cc. of a 9:1 AcOEt-MeOH mixt. was decolorized with Carboraffin, evapd., dissolved in 25 cc. AcOEt and treated cautiously with petr. ether (so as not to effect a permanent cloudiness) yielded 1.5 g. anhyd. 2,4-dibenzyl-3-(tribenzylgalloyl)glucose (IX), m. 115°, [α]₂₀D 6.7 ± 1° (c 2.1, MeOH). A soln. of IX in MeOH evapd. and allowed to crystallize gave IX·3H₂O (IXa) (recrystd. from aq. MeOH or Me₂CO), [α]₂₀D 5.7 ± 1° (c 2.1, MeOH). IXa on a block preheated to 90°, melted instantly. IXa heated gradually softened 90-95°, m. 112°. Dry IX (1.53 g.) and 2.14 g. IIa in 7.6 cc. pyridine were kept 50 days at 60°, evapd., dried over H₂SO₄, dissolved in 50 cc. C₆H₆, washed with aq. NaHCO₃ and H₂O, dried, concd. to 25 cc., seeded with III, kept 24 hrs. at 20°, filtered, dild. with 40 cc. C₆H₆ and chromatographed on IIIa to give 320 mg. 1,3,6-tris(tribenzylgalloyl)-2,4-dibenzylglucose (X), C₁₀₄H₉₀O₁₈, microneedles, m. 144° (AcOEt), [α]₂₀D 24.2 ± 0.5° (c 2, AcOEt). X (0.65 g.) hydrogenated in 90 cc. AcOEt and 30 cc. MeOH, with 0.3 g. Pd gave 250 mg. foam, which in 4 cc. 50% Me₂CO was treated with C, and freed from Me₂CO, giving 1,3,6-trigalloyl-β-D-glucose, [α]₂₀D 29.5 ± 1.5° (c 2.2, abs. EtOH), R_f 0.38, identical with the natural product described in the preceding part. VIII (2.34 g.) in 53 cc. C₆H₆ with 2.53 g. dry III was treated with 11 cc. (CF₃CO)₂O and 1.64 cc. soln. VIIIA, kept 24 hrs. at 20°, poured into ice-H₂O, and extd. with 1:2 AcOEt-Et₂O. The washed and dried org. phase, decolorized with C, was evapd., taken up in 100 cc. C₆H₆, kept 24 hrs. (thus freed from most III), filtered, evapd., refluxed 1 hr. with 20 cc. MeOH, evapd. dissolved

in 50 cc. C₆H₆, and chromatographed on IIIa, give 0.5 g. 2,4-dibenzyl-3,6-bis(tribenzylgalloyl)glucose, m. 132-4°, [α]_{20D} 29° (c 2, AcOEt), showing no mutarotation, giving, on paper a reddish-brown coloration with PhNH₂ acid phthalate. The significance of the various reactions, in terms of the configuration of the compds. is discussed.

CC 10 (Organic Chemistry)

L57 ANSWER 8 OF 20 HCA COPYRIGHT 2004 ACS on STN

51:66529 Original Reference No. 51:12040i,12041a-i,12042a-g Natural tannins. XXIV. Synthesis of octamethylvaloneic acid. Schmidt, Otto Th.; Komarek, Ernst; Rentel, Heinz (Univ. Heidelberg, Germany). Ann., 602, 50-60 (Unavailable) 1957.

AB cf. C.A. 50, 2487h. All m.ps. were taken with the Bock Monoscope app. and were cor. Most compds. were dried over P₂O₅ at 0.4 mm. and appropriate temps. Chromatograms were made on Schleicher and Schull papers rendered hydrophobic by immersion in 3 or 10% silicone oil (AK 1000, Wacker-Chemie) dissolved in cyclohexane, and dried in air; those areas of the papers that were to be immersed in the solvent trough were left untreated. The chromatographic tanks were kept satd. with CHCl₃ vapor before the CHCl₃-satd. solvent (consisting of H₂O contg. 2% AcOH and 1% MeOH) was introduced into the trough. Chromatograms were run at 10°, and after drying were developed either by spraying with 2-HO₂SC₆H₄N₂Cl (when free phenolic OH groups were present) or else treated 3 min. with Br vapor and 20 min. with NH₃ and then viewed under ultraviolet (U.V.) light. Extensive (qual.) soly. data are given. Tetraacetyllellagic acid (I) (12 g.) and 20 g. recently ignited K₂CO₃ in pure BzMe was **stirred** 6 hrs. at 125-30°, cooled, filtered, washed with a little MeOH, suspended in 400 cc. H₂O, and acidified with 18% HCl; the ppt. washed with H₂O, MeOH, and Et₂O gave 6 g. 4,4'-diacetyllellagic acid (II), prisms, not m. at 350°. II gave no color with FeCl₃, and responded negatively to the Griessmayer-Reichel (G.-R.) reaction for ellagic acid. The 3,3'-di-Me deriv. (III) of II, prisms, m. 302-5° (from HCONMe₂ or dioxane). Sapon. of 5 g. III by refluxing 2 hrs. with 2N KOH in MeOH (preferably under H) followed by diln. with H₂O and acidification with 2N H₂SO₄ gave 3.2 g. 3,3'-dimethylellagic acid (IV), pale yellow, m. 319-20° (from HCONMe₂ or dioxane), giving neither the FeCl₃ nor the G.R. reaction. In hot dioxane IV gave reddish violet colorations with active PbO. Crude II (12 g.) was freed from part of the ellagic acid (V) by extg. with hot MeOH, methylated with CH₂N₂, and sapond. first with 2N KOH in MeOH and then with aq. N KOH, filtered, and the filtrate acidified with 18% HCl giving almost exclusively V, the filtrate from which was heated, giving 3.8 g. IV. To BzMe (400 cc.), 21 g. IV, and 60 g. dry K₂CO₃ **stirred** and heated at 140° was added 100 cc. PhCH₂Cl in 10 portions every 30 min. More rapid

addn. caused losses in yield. After heating 2 hrs., the cooled product was washed with MeOH and H₂O giving 27.3 g. 4,4'-dibenzyl deriv. (VI) of IV, **hexagons**, m. 295-6° (when preheated to 280°) (from BzMe or HCONMe₂). To 5.2 g. VI in 50 cc. boiling 2N KOH in MeOH, H₂O was added dropwise until the soln. was clear, MeOH was removed in vacuo, another 30 cc. H₂O added, and the filtered mixt. at 0° acidified with HCl giving 4.1 g. 2,2'-dihydroxy-3,3'-dimethoxy-4,4'-dibenzoyloxy-6,6'-dicarboxybiphenyl (VII), long needles, readily lactonized and showing no definite m.p. (from Me₂CO by addn. of petr. ether); the 2,2'-di-MeO analog (VIII) of VII, prismatic rods, m. 236° (from MeOH), was formed by treating VI with aq. 2N NaOH, methylating with Me₂SO₄, pptg. with HCl, and sapon. any residual ester with KOH in MeOH. The di-Me ester (IX) of VIII, **hexagons**, m. 145° (from MeOH, Me₂CO, or C₆H₆petr. ether) was formed by methylating IX in MeOH or VII in Me₂CO with excess CH₂N₂ in Et₂O; under these conditions, in one instance, another cryst. compd. (X), a lactone analog of VIII, m. 185°, was formed. VI (37 g.) in 200 cc. MeOH was **stirred** and refluxed 0.5 hr. with 2N NaOH and treated dropwise with 500 cc. H₂O. MeOH and 100 cc. H₂O was distd. and the filtered mixt. **stirred** and treated at 35° with Me₂SO₄ until a spot test coloration with HO₂SC₆H₄N₂Cl was neg., then warmed to 60°, treated with 20 cc. 25% NaOH, heated 0.5 hr. at 95°, cooled, acidified with concd. HCl, and the resulting ppt. remethylated with CH₂N₂ in Et₂O giving 39 g. IX. By prehydrogenating 0.3 g. PdCl₂ in abs. MeOH, a catalyst was prepd. which was used in the 48 hr. hydrogenation at 40° of 38 g. IX suspended in 200 cc. MeOH giving 25 g. 4,4'-dihydroxy-2,2',3,3'-tetramethoxy-6,6'-carbomethoxybiphenyl (XI), rodlets, m. 135° (from C₆H₆-petr. ether); free acid (XIa), **hexagons**, m. 283-4° (from aq. dioxane or tetrahydrofuran-petr. ether and dried at 135°/1 mm. over P₂O₅ and paraffin). 4,4'-Dihydroxybiphenyl (4.4 g.) in 30 cc. 2N NaOH was **stirred** with 3.5 cc. Me₂SO₄, after 0.5 hr. warmed to 80°, and any di-Me ether ppt. filtered off and washed with NaOH. The filtrate, acidified with 2N HCl, was boiled, filtered hot, and the ppt. washed with hot H₂O, dried, dissolved in hot 2N NaOH, and cooled to 0° giving an insol. Na compd. which was washed (at 0°) with 2N NaOH, suspended in H₂O, acidified with 2N HCl, heated, filtered, and the ppt. washed with H₂O to neutrality giving 3.8 g. 4-hydroxy-4'-methoxybiphenyl, leaflets, m. 186° (from Bu₂O or aq. dioxane). [4,3,5-(HO)(MeO)2C₆H₂]₂ (XII) (hydrocoerulignone) (3.8 g.) was partially methylated in 50% dioxane under H using 2N KOH and 4 g. Me₂SO₄ at 10°. The mixt., acidified to pH 5-6, was poured into 900 cc. H₂O, cooled to 0°, and the pptd. 4,4'-di-Me deriv. of XII filtered off. The filtrate evapd. in vacuo to incipient crystn. was cooled to 0° giving about 1.05 g. 4'-Me

deriv. of XII, m. 146° (by successive crystn. from MeOH, C₆H₆-petr. ether with C, and EtOH, followed by cold-finger sublimation at 135°/0.01 mm.), turning pink on exposure to air. XI (3 g.) in 21 cc. 66% dioxane at 30° methylated with 2N NaOH and Me₂SO₄, acidified with 2N H₂SO₄, extd. with Et₂O, the ext. washed with aq. NaHCO₃ and H₂O, and dried gave a sirup, which in CHCl₃ was chromatographed on alkali-free Woelm Al₂O₃. Elutions with CHCl₃ were monitored by use of U.V. light. Three zones were noted, the fastest-moving one (di-Me hexamethoxydiphenate) was eluted completely with CHCl₃. The column was cut between the remaining 2 zones, and each section was extd. with MeOH. These exts. were examd. by paper chromatography; the upper zone yielded XI. The central zone gave largely th 4-Me deriv. of XI (frequently contaminated with XI). Further sepn., described in detail, permitted the isolation of 1.7 g. 4-Me deriv. of XI, rhombs, m. 84° (after seeding the MeOH soln., and subsequent crystn. from C₆H₆-petr. ether and 50% MeOH), sapon. of which gave 91% 4-Me deriv. of XIa, rhombs, m. 247° (from Me₂CO and aq. dioxane). The 4-Me deriv. of XI (1 g.) with 3.3 g. 2,3,4,5-Br(MeO)₃C₆HCO₂H (cf. Mayer and Fikentscher, C.A. 50, 14643i) in 10 cc. dry MeOH was treated with 3.1 cc. 4.4N MeOK, evapd. in vacuo, heated 2 hrs. at about 100°/14 mm., powdered and dried 16 hrs. at 1 mm. over "Blaugel," mixed with 0.75 g. defatted Natur Cu C and 40 mg. Cu(OAc)₂, dried at 40°/0.4 mm. over P₂O₅ in a test tube placed in a drying pistol, after which the former was removed, connected with a "Blaugel" tube and heated 2 hrs. at 125-30°, cooled, repowdered rapidly, retreated with 0.1 g. Natur Cu C, and heated 2 hrs. at 170-80°. The product, taken up in the min. amt. 2N NaOH, was filtered and the filtrate heated 1 hr. on a steam bath, acidified with 18% HCl, the amorphous ppt. taken up in MeOH, esterified with CH₂N₂, evapd., the sirup in CHCl₃ chromatographed on Woelm Al₂O₃, and eluted with CHCl₃ until the fastest moving area, fluorescing brilliantly in U.V. light, was removed. The evapd. eluate, a mixt. of Me trimethylgallate, di-Me hexamethoxyphenate, and tri-Me octamethylvaloneate, was fractionated in high vacuum; (MeO)₃C₆H₂CO₂Me, b_{0.01} 95-7°; di-Me hexamethoxyphenate, b_{0.01} 200° (bath temp.). The distn. was interrupted after 15 min. at 240°/0.01 mm. and the resulting brown still residue purified by soln. in CHCl₃ and chromatographing on Al₂O₃ (as above), evapg., and heating in vacuo at 200-250°, and then repeating the chromatographic procedure. The sirup resulting from the final CHCl₃ eluate was sapond. with 2N KOH in MeOH, treated slowly with H₂O, acidified, and the ppt. washed with H₂O, and dried giving 425 mg. octamethylvaloneaic acid, 4',5,5',6,6'-hexamethoxydiphenic acid 4-(4,5,6-trimethoxy-2-carboxyphenyl) ether, m. 250°, identical crystallographically and in its soly. with the compd. prepd. previously from a natural product, and showing no m.p. depression when mixed with this compd.

CC 10 (Organic Chemistry)

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51:25257 Original Reference No. 51:4952b-i,4953a-c Amino sugar syntheses. IV. The preparation of N-acetyllactosamine (4- β -D-galactopyranosyl-2-deoxy-2-acetamino-D-glucopyranose) from lactose. Kuhn, Richard; Kirschenlohr, Werner (Max-Planck-Inst. Med. Forsch., Heidelberg, Germany). Ann., 600, 135-43 (Unavailable) 1956.

AB Lactose hydrate (I) (180 g.) at 65° yielded 159 g. oxime (II), rhombs, m. 183-5°, $[\alpha]_{D22}$ 38.3° \rightarrow 15.5° (after 25 hrs., c 1, H₂O), 7 g. of which in 70% MeOH with ketene (0.2 mole), after evapn. and cooling, gave 2.5-3.0 g. N-Ac deriv. of II, m. 230-2° (decompn.) (from aq. MeOH), $[\alpha]_{D23}$ 14.1° \rightarrow 16° (after 12 hrs., c 1, H₂O). The infrared spectrum shows the C:O band characteristic of N-Ac; no N-O-Ac band (at 5.55 μ) was present. I (180 g.) in 300 cc. H₂O and 100 cc. MeOH was converted to II, which as a sirup (without isolation) dissolved in 200 cc. pyridine was added dropwise at 100° to 180 g. anhyd. AcONa in 1.2 l. Ac₂O. After 1 hr. the cooled mixt. was **stirred** into 8 l. ice H₂O, the ppt. washed with cold H₂O, dissolved in 750 cc. EtOH and again **stirred** with 8 l. ice H₂O giving 270-300 g. crude octaacetyllactobionic acid nitrile (III), C₂₈H₃₇O₁₈N.C₆H₆, **hexagons** (from C₆H₆), m. 90-3° $[\alpha]_D$ 35.5° (c 1.3, MeOH), losing C₆H₆ on long drying at 75°/5 mm over P205-paraffin. III (20-22 g.) was also formed from 18 g. purified II by heating on a steam bath with AcONa and Ac₂O. To 75 g. III in 350 cc. MeOH and 200 cc. M MeONa, after 10 min. at 20°, was added 110 cc. 2N AcOH followed by immediate concn. in vacuo to 110 cc. and addn. of 100 cc. H₂O, passage through Amberlite IR-120, and evapn. of the eluate to a sirup from which AcOH was removed by repeated evapns. with H₂O. The final sirup with 30 cc. MeOH, after 48 hrs. (especially on seeding), gave 18-20 g. 3- β -D-galactosyl-D-arabinose (IV), m. 162-9°, $[\alpha]_{D23}$ -54.5° \rightarrow -62° (after 7 hrs., c 1, H₂O); the mother liquors yielded another 2-3 g. IV isolated as N-phenyl(3- β -D-galactosyl-D-arabinosyl)amine (V). IV (6.2 g.) **stirred** 1.5-2 hrs. under reflux on a steam bath with 120 cc. EtOH, 2 g. PhNH₂, and 50 mg. NH₄Cl, and cooled gave 6.9 g. crude V, which, recrystd. from EtOH-H₂O gave V.H₂O, rodlets, m. 170-1°, $[\alpha]_{D22}$ 34.7° (c 0.8, pyridine); the $[\alpha]_{D22}$ 36° (HCONMe₂), decreased imperceptibly at first to 7.5° (after 96 hrs., c 1.03); $[\alpha]_{D22}$ -16° (10 min.) \rightarrow -42° (after 1 hr., c 0.93, H₂O). H₂O effects very rapid hydrolysis of V to PhNH₂ and IV. V could be readily prepd. from sirups contg. IV (made from III). Also formed from such sirups, by the use of appropriate

amines, were the following (3- β -D-galactopyranosyl-D-arabinosyl)amines: N-p-tolyl-H₂O, m. 162-4°, [α]D₂₂ 11.4° (10 min.) \rightarrow 0° (5 hrs., c 1.1, pyridine); N- α -naphthyl-H₂O, m. 196-8° (decompn.), [α]D₂₃ 842° (20 min., c 0.57, HCONMe₂); N- β -naphthyl, 167-9° (decompn.), [α]D₂₃ 21.5° (4 min.) \rightarrow 6.5° (48 hrs., solvent not given); N-benzyl (VI), m. 125-6° (sintering 107°), [α]D₂₂ -20° (5 min.) \rightarrow -29° (24 hrs., c 0.95, pyridine). V in hot H₂O, heated 20 min. with BzH, after Et₂O extn., gave IV in the aq. phase. V (35-40 g.) was also formed as follows (cf. Frush and Isbell, C.A. 48, 8740a): 100 g. Ca lactobionate-H₂O, 5 g. (AcO)₂Ba, and 2.5 g. FeSO₄·7H₂O was **stirred** in 750 cc. boiling H₂O, cooled to 35°, **stirred** with 30 cc. 30% H₂O₂ (below 40°) and, after 45 min., with 30 cc. H₂O₂. After 3 hrs., the filtered soln. was evapd. to a thin sirup, 500 cc. MeOH added very gradually, and the pptd. Ca salts filtered off; the filtrate, treated with 9% (CO₂H)₂ was centrifuged, and the soln. passed through Amberlite IR-45, evapd. in vacuo, and treated with MeOH and PhNH₂ giving V. In place of (CO₂H)₂, suitable ion-exchangers could be used. V (40 g.) in 150 cc. HCONMe₂ and 8 cc. HCN warmed 1-2 hrs. at 80° was retreated with 6 cc. HCN, and after 2.5 hrs. evapd. to a sirup, treated with MeOH, reevapd., treated with 100 cc. H₂O and 110 cc. 2N HCl, and hydrogenated 24 hrs. as above (taking up 3 moles H), centrifuged, extd. with Et₂O to remove cyclohexanone, **stirred** with Amberlite IR-45, and the filtrate evapd. to a sirup, treated with 17.2 g. anhyd. AcONa (or 28 cc. Et₃N) in 160 cc. 50% MeOH, cooled, kept 24 hrs. at 20° with 24 cc. Ac₂O, evapd., dissolved in 130 cc. H₂O, passed through Amberlite IR-120, the eluate neutralized with Amberlite IR-45, filtered, decolorized with C, evapd., treated with 100 cc. MeOH, and kept 48 hrs. at 0° giving 17-18 g. N-acetyllactosamine (VII) (4- β -D-galactopyranosyl-N-acetyl-D-glucosamine), C₁₄H₂₅O₁₁N·MeOH, m. 168-7°, [α]D₂₂ 50.5° \rightarrow 28.5° (c 1, H₂O), identical with the compd. isolated from the blood group components of Meconium (Kuhn and Kirschenlohor, C.A. 49, 4069b). VII (1.4-1.6 g.) was also prepd. analogously from 4.02 g. VI. To 6.2 g. VII in 75 cc. H₂O and 250 cc. MeOH at 0° was added freshly distd. CH₂N₂ from 40 g. MeN(NO)CONH₂ (VIII), kept 12 hrs., evapd., dissolved in 50 cc. H₂O and 120 cc. MeOH, retreated with CH₂N₂ (from 20 g. VIII), kept 24 hrs., evapd., and treated with 10 cc. MeOH giving, after 24 hrs., 0.65 g. β -methyl-N-acetyllactosaminide (4- β -D-galactopyranosyl-2-deoxy-2-acetamino- β -methyl-D-glucopyranoside) (IX), m. 234-5° (decompn.), [α]D₂₂ -23.1° (c 0.86, H₂O); the mother liquors chromatographed showed both IX and VII by the chlorobenzidine reaction (Rydon and Smith, C.A. 46, 11290b). When CH₂N₂ was not distd. prior to use, these mother liquors showed the

presence of another compd., probably the α -isomer of IX.
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51:5404 Original Reference No. 51:1123a-i,1124a-c Acid-catalyzed reaction of 9-fluorenol with 9-alkylidenefluorenes. Wawzonek, S.; Dufek, E. (State Univ. of Iowa, Iowa City). Journal of the American Chemical Society, 78, 3530-3 (Unavailable) 1956. CODEN: JACSAT. ISSN: 0002-7863.

AB Fluorenone (180 g.) in 300 cc. dry C₆H₆ added to 1 mole PrMgBr in 300 cc. dry Et₂O and 300 cc. dry C₆H₆, and the mixt. refluxed 3 hrs. and decompd. with NH₄Cl gave 130 g. crude 9-propyl-9-fluorenol (I), m. 90-100°; the I heated 2 hrs. with 500 cc. glacial AcOH and 50 cc. concd. HCl, and dild. with an equal amt. cold H₂O, the aq. layer extd. with petr. ether, and the combined org. layer and ext. worked up gave 56.1 g. 9-propylidenefluorene (Ia), b₁ 150-5°; the dark glassy distn. residue crystd. from EtOAc, and the resulting orange solid recrystd. successively from C₆H₆, EtOAc, and CCl₄ yielded 2.5 g. 1-(9-fluorenyl)-1-(9-fluorenylidene)propane (II), m. 162-4° (from EtOAc); the MgSO₄ used for drying the original soln. of the reaction products treated with H₂O and extd. with C₆H₆ gave an addnl. 16.5 g. II. The crude I recrystd. twice from MeOH gave pure I, m. 125-6°; the MeOH filtrate dild. with H₂O gave 11.7% 9-fluorenol (III), m. 149-51° (from C₆H₆). III (4.5 g.) and 5.5 g. Ia in 30 cc. glacial AcOH and 3 cc. concd. HCl refluxed 1.25 hrs., cooled, and treated with 10 cc. cold H₂O, and the yellow gummy product crystd. from EtOAc yielded 2.5 g. II, m. 160-2°. Similar results were obtained using a mixt. of I and III. Crude 9-butyl-9-fluorenol (30 g.) heated with glacial AcOH and concd. HCl in the usual manner gave 21.8 g. 9-butylidenefluorene and 1 g. butane analog of II, white **hexagonal** plates, m. 158-60° (from C₆H₆-petr. ether and EtOAc). III (4.5 g.) and 5.5 g. 9-ethyl-9-fluorenol refluxed with glacial AcOH and concd. HCl gave 8.0 g. ethane analog (IV) of II, m. 139-41° (from EtOAc, CCl₄, and EtOAc). III (4.5 g.) and 5.5 g. 9-methyl-9-fluorenol gave similarly 4.0 g. 9-fluorenyl-9-fluorenylidene methane (V), m. 206-8° (from C₆H₆-petr. ether and EtOAc). II (1 g.) in 50 cc. glacial AcOH refluxed 1.75 hrs. with 47% HI (d. 1.50) yielded 0.63 g. ethyldi(9-fluorenyl)methane, long white needles, m. 158-60° (from C₆H₆-petr. ether). V (0.20 g.) gave similarly 0.15 g. di(9-fluorenyl)methane (VI), long white needles, m. 212-13° (from C₆H₆-petr. ether). 9-Chloromethylfluorene (VII) (0.8 g.) in ligroine (b. 60-8°) added to 9-fluorenyllithium from 1 g. Li and fluorene (VIII), the mixt. refluxed 12 hrs., decompd. with abs. EtOH, and steam distd., and the distn. residue triturated with hot EtOH gave 0.6 g. VI, m. 212-13° (from C₆H₆-petr. ether). 9-Fluorenylcarbinol (15 g.) refluxed 0.5 hr. with 45 cc. SOCl₂ and distd. gave 5.6 g. VII, m.

66.5-7.5° (from EtOH), b1-3 140-5°; the crude product from another run dissolved in Et2O and washed with H2O yielded 100% bis(9-fluorenylmethyl) sulfite, m. 106-7°. II (1.0 g.) in EtOAc treated at -40° with ozone, the soln. treated with H (40 lb.) in the presence of PtO2, and the solvent removed yielded 0.05 g. of Et 9-fluorenyl ketone, m. 93-6° (from EtOH); a similar ozonide soln. decompd. with Pd catalyst gave only III, m. 149-51°, and fluorenone (VIIIa) (2,4-dinitrophenylhydrazone, m. 300° decompn.). II (0.20 g.) in 20 cc. glacial AcOH refluxed 1 hr. with 1.2 g. K2Cr2O7 and 1 cc. concd. H2SO4, cooled, and dild. with 50 cc. H2O gave 0.15 g. VIIIa, m. 80-3°. II (0.5 g.) in 10 cc. C6H6 and 15 cc. 98-100% HCO2H kept 36-48 hrs. at room temp. with 2 cc. 30% H2O2 yielded 0.35 g. Et 9-(9,9'-bifluorenyl) ketone (IX), m. 211-12° (from aq. EtOH). IV oxidized in the same manner gave the Me ketone analog of IX, m. 160-1° (from EtOH). IX (0.3 g.) refluxed 3 hrs. with KOEt from 3.3 g. K in 20 cc. EtOH and cooled deposited 0.2 g. 9,9-bifluorenyl, long white needles, m. 244-5° (from C6H6 and petr. ether). Liquid NH3 (15 cc.) added to 1.9 g. 9-chlorofluorene and 2.2 g. Et 9-fluorenyl ketone (X) in 10 cc. dry PhMe, allowed to stand overnight, and evapd. in vacuo yielded 0.8 g. IX, m. 212-13° (from 95% EtOH). KOMe from 10.5 g. K, 43 g. VIII, and 27.6 g. EtCO2Et in 80 cc. Et2O refluxed 20 hrs., poured into 225 cc. H2O, acidified with 3N HCl, and extd. with Et2O yielded 24.6 g. X, long white needles, m. 101°; 2,4-dinitrophenylhydrazone, m. 170-70.5° (from EtOH). IX (0.5 g.) in 10 cc. abs. Et2O added to 0.2 g. LiAlH4 in 20 cc. abs. Et2O, decompd. with EtOAc and dil. HCl, and worked up in the usual manner gave 0.3 g. ethyl-9-(9,9'-bifluorenyl)carbinol, m. 181-2° (from C6H6-petr. ether). VIII (27.7 g.) in 85 cc. xylene added to 0.42 mole EtMgBr in 300 cc. Et2O, refluxed 3 hrs. while distg. off slowly the Et2O, the residual xylene soln. treated with 50 cc. Et2O and 50 cc. xylene, the resulting solid refluxed 2.5 hrs. with 4.8 g. EtCO2Et in 50 cc. Et2O, and the mixt. decompd. with NH4Cl and extd. with Et2O yielded 3.2 g. VIII; the remaining oil distd. yielded 0.8 g. mixt. of Ia and X, b1 132-8°, and 0.5 g. X, b1 138-45°, m. 101°; the dark red distn. residue crystd. from EtOAc yielded 1.0 g. II, m. 161-4°. 9-Carbethoxy-9,9'-bifluorenyl (2.2 g.) in 30 cc. dry Et2O **stirred** 1 hr. with 1.2 g. LiAlH4, treated with excess EtOAc, and acidified with dil. HCl, and the Et2O layer worked up gave 1.1 g. 9-(9,9'-bifluorenyl)carbinol (XI), white crystals, m. 174-5°. XI (1.0 g.) in 20 cc. dry xylene refluxed 4 hrs. with 5.0 g. P2O5, the soln. cooled and decanted, the residue extd. with a small amt. of hot C6H6, the combined C6H6 and xylene solns. washed, filtered, and evapd. to dryness in vacuo, and the residue recrystd. twice from C6H6-petr. ether gave 0.64 g. 9-(9'-fluorenyl)phenanthrene, m. 196-8°. I (2.5 g.) in 40

cc. warm glacial AcOH treated with 80 cc. SnCl₂-iodine soln. (prepd. by adding 10 g. SnCl₂ in 20 cc. concd. HCl to 5 g. iodine in 80 cc. warm glacial AcOH), the mixt. **stirred** 1.5 hrs., and the orange ppt. crystd. from Et₂O gave 0.9 g. 9,9'-dipropyl-9,9'-bifluorenyl, white crystals, m. 208-9°. 9-Butyl-9-fluorenyl (2.5 g.) gave similarly with SnCl₂ and iodine 0.8 g. 9,9'-dibutyl-9,9'-bifluorenyl, m. 202° (from EtOAc).

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51:1788 Original Reference No. 51:387c-i,388a-i,389a Condensation products of phenols and ketones. X. The structure of Dianin's compound, a unique inclusion-forming substance. Baker, Wilson; Floyd, A. J.; McOmie, J. F. W.; Pope, G.; Weaving, A. S.; Wild, J. H. (Bristol Univ., UK). Journal of the Chemical Society, Abstracts 2010-17 (Unavailable) 1956. CODEN: JCSAAZ. ISSN: 0590-9791.

AB cf. C.A. 47, 8678b. A product, "Dianin's compd.," 1st prepd. in 1914 (cf. C.A. 9, 1903), from PhOH and Me₂C:CHCOMe, is shown to be 4-p-hydroxyphenyl-2,2,4-trimethylchroman (I). Oxidation yields 2,2,4-trimethylchroman-4-carboxylic acid (II), and thermal degradation gives PhOH and 2,2,4-trimethylchromene (III). The latter compd. has been synthesized and yields I by addn. of PhOH. I forms inclusion compds. with over 50 widely different org. solvents, some inorganic gases and with iodine. The large, separate cavities in the crystals are defined by six mols. of I and the ratio of no. of mols. of I to the no. of included mols. is generally 6:1, though a ratio of 3:1, i.e., 2 mols. per hole, is found for a no. of small mols. PhOH (400 g.) and 100 g. Me₂C:CHCOMe was satd. 8 hrs. with a stream of anhyd. HCl, the resulting red viscous mixt. kept dry 4 days at 38°, then 1 l. boiling H₂O added, the mixt. well shaken and heated on a water-bath, the top aq. layer decanted and lower layer similarly treated with 1 addnl. l. hot H₂O and decanted, the resulting oily product shaken with 250 ml. hot EtOH, cooled, the resulting cryst. EtOH adduct collected, and twice **stirred** with 150 ml. portions cold EtOH yielding 115-30 g. (40-5%) **hexagonal** crystals, m. 165-6° after crystn. from EtOH. The EtOH complex (30 g.) was dissolved in 200 ml. hot 2N NaOH, boiled 15 min., CO₂ passed through for 30 mins., the ppt. boiled twice with 200 ml. portions H₂O, and dried in vacuo over P₂O₅ yielding 26 g. I, fine needles, m. 156-7°. The EtOH complex was also slowly sublimed at 140°/0.1 mm. yielding unsolvated I, large irregular prisms, m. 155-6°. I is sol. in hot aq. KOH and on cooling gave a crystn. alkali salt. A satd. boiling soln. of KMnO₄ in 1200 ml. Me₂CO was added rapidly to a soln. of 3 g. EtOH adduct of I in 100 ml. Me₂CO contg. a few crystals of FeSO₄, the Me₂CO removed by distn., the residue shaken with 100 ml. H₂O, 20 g. Na₂S₂O₅, and 20 ml. 2N HCl, and SO₂ passed through until all the MnO₂ had dissolved, the mixt. then extd. with

3 + 50 ml. Et₂O, the Et₂O exts. shaken 3 times with satd. aq. Na₂CO₃, the alk. soln. acidified, the resulting ppt. boiled with 4 + 30 ml. petr. ether, the petr. ether ext. concd. to 5 ml., and cooled to 0° yielded a sticky solid; 2 crystns. from the same solvent gave 0.16 g. II, irregular prisms, m. 124-5°. II, on treatment with cold concd. H₂SO₄, dissolved slowly with evolution of CO, at 40°, the reaction was brisk. The nonacidic material in the oxidation with 2,4-dinitrophenylhydrazine in alc. H₃PO₄ gave the 2,4-dinitrophenylhydrazone of 2,2-dimethylchromanone, orange-red needles, m. 222-3°. Methylation of the EtOH adduct of I, suspended in Me₂CO, with excess Me₂SO₄ and KOH gave 87% ether, b_{0.5} 140-1°, which solidified after 4 weeks as rectangular tablets, m. 50-1° (from petr. ether). The tribromo deriv., needles, prepd. at room temp. with excess Br and AcOH during 18 hrs., m. 103-4° (from EtOH). The EtOH adduct of I (40 g.) was refluxed 2 hrs. at 300° yielding an oil which was twice distd., shaken with 100 ml. 10% NaOH, and extd. with 3 + 50 ml. Et₂O yielding 18.5 g. III, b₁₇, 114-15°, n_D²⁰ 1.5502. III (0.5 g.) was treated dropwise at room temp. with 3 ml. Br, left overnight, the semi-solid product dissolved in CHCl₃, the soln. shaken with aq. NaHSO₃, dried, the residue crystd. twice from petr. ether yielding 1.18 g. 3,3,4,6,8-pentabromo-2,2,4-trimethylchroman, rectangular prisms, m. 145-6°. Excess satd. aq. KMnO₄ was dropped into a stirred suspension of 2 g. III in 20 ml. 1% aq. KOH, the soln. acidified, decolorized with SO₂, then satd. with NaCl, and extd. with Et₂O, and resulting oil gave a 2,4-dinitrophenylhydrazone of o-(2-formyl-1-methylethoxy)acetophenone, orange-red plates, m. 203-4° (from MeOH). Similar results were obtained by the oxidation of 1 g. III with 3 g. Cr₂O₃ in 10 ml. H₂O and 20 ml. AcOH. III (1 g.) was also ozonized 1 hr. at -20° in 20 ml. dry CCl₄, the solvent removed in vacuo, and the oil isolated as usual giving the o-hydroxyacetophenone; 2,4-dinitrophenylhydrazone, m. 212-13° (from EtOH). β,β-Dimethylacryloyl chloride (7.5 g.) was added dropwise to 6 g. PhOH, the mixt. heated 4 hrs. on a steam-bath, cooled, 100 ml. H₂O added, and the oily product extd. with Et₂O giving 8.8 g. phenyl β,β-dimethylacrylate, b₁₁ 127°. This ester (2 g.) was slowly added to 2.1 g. powd. AlCl₃, the mixt. heated 2 hrs. at 90° cooled, 25 ml. 2N HCl added, the mixt. extd. with Et₂O, and the Et₂O ext. washed with 1% NaOH and H₂O yielding 0.9 g. 2,2-dimethylchromanone (IV), prisms, m. 87-8° (from petr. ether); 2,4-dinitrophenylhydrazone, m. 220-1° (from EtOH). 4-Methylcoumarin (10 g.) in 200 ml. Et₂O was added during 1 hr. to MeMgI prepd. from 12.2 g. Mg and 71 g. MeI in 100 ml. Et₂O, the mixt. boiled 10 hrs., then poured into 200 ml. 20% HCl contg. 200 g. ice, extd. with Et₂O and the partial solid crystd. from petr. ether yielding 1.2 g. 4-o-hydroxyphenyl-2-methylpent-3-en-2-ol (V), needles, m. 97-8°. V, on distn.

gave 73% III, b28 124-6°, nD20 1.5511, and the same pentabromide, m. 145-6°. V (0.8 g.) was cyclized by boiling 0.5 hr. with 10 ml. AcOH and 0.25 ml. concd. H2SO4, the soln. dild. with H2O, the product collected in Et2O and dist. yielding 0.48 g. IV. Dry HCl was bubbled 1 hr. through a cooled mixt. of 1.65 g. PhOH and 1.5 g. IV, and after 5 days the cryst. mass worked up as before giving 1.23 g. EtOH adduct of I, m. 163-4°; benzoate, m. 160-1° (from EtOH). A mixt. of 2.25 g. o-cresol and 2.5 g. III was satd. with HCl for 1 hr., after 12 days the partly cryst. mass extd. with 5 + 20 ml. boiling H2O, the residue steam dist., and the residue collected in Et2O yielding 2.4 g. 4-(4-hydroxy-3-methylphenyl)-2,2,4-trimethylchroman, needles, m. 135-6°; acetate, irregular prisms, m. 121-2°. Cryst. adducts of I were prepd. by crystn. of unsolvated I from the various liquid solvents. With MeI, I was placed in the thimble of a Soxhlet app. and extd. with MeI, the adduct sepd. as the solvent became satd. The iodine adducts were prepd. by using decalin as solvent. With NH3 and SO2, I was dissolved in the liquified gases, and the solns. decanted from the undissolved solids and allowed to evaporate. The adducts were analyzed by drying the complexes 4 hrs. at 100°/0.1 mm., then weighed samples heated 5-10 min. at 190-200° and again weighing. Samples of the adducts with aliphatic acids were dissolved in EtOH and titrated with 0.02N NaOH. The iodine adduct in EtOH was titrated with 0.01N Na2S2O3. Cryst. adducts of I, with solvent used, m.p., and moles I/mole solvent were: MeOH, 155-6°, 2; EtOH, 163-4°, 3; iso-PrOH, 160-1° 3; BuOH, 159-60°, 3; tert-BuOH, 166-7°, 3; Me2CO, 159-60°, 3; CCl4, 159-60°, 3; CH2Cl2, 167-8°, 3; MeI, 166-7° 3; MeNO2, 164-5°, 3; HCO2H, 159-60°, 3; AcOH, 161-2°, 3; EtCO2H, 156-7°, 4; CHCl3, 161-2°, 4; CS2, 164-5° 4; C3H7CO2H, 162-3° 5; AmOH, 169-70°, 6; C6H13OH, 162-3°, 6; Et2O, 172-3° 6; BrCH2CH2CH2Br, 168-9° 6; C2H4Cl2, 163-4°, 6; C2H4Br2, 165-6°, 6; CCl2:CCl2, 153-4°, 6; BuBr, 169-70°, 6; biacetyl, 162-3°, 6; C4H9CO2H, 169-70°, 6; C5H11CO2H, 160-70°, 6; Et2NH, 164-5°, 6; CH2ClCO2Et, 171-2°, 6; C6H6, 160-1°, 6; PhMe, 155-6°, 6; o-MeC6H4OH, 154-5°, 6; m-MeC6H6OH, 153-5° 6; p-MeC6H4OH, 152-3°, 6; PhBr, 158-9°, 6; PhI, 152-4°, 6; o-ClC6H4Cl, 150-1°, 6; diisobutylene, 157-8°, 7; tert-AmOH, 161-2°, 7; AcOEt, 167-8°, 7; C4H9CO2Am-iso, 160-1°, 7; p-BrC6H4OMe, 154-5° 7; m-ClC6H4Cl, 158-9°, 7; 2-bromopyridine, 154-5°, 7; 2,6-lutidine, 164-5°, 7; 3-methylheptane, 174-5°, 8; 1-MeClOH7, 157-8° 8; pyridine, 159-60°, 8; Et3N, 158-59°, 9; Decalin, 157-8°, 9; Decalin, 150-7° 17; SO2, 152-3°, 4; NH3, 161-2°, 6; and iodine, 154-5°, 7.

CC 10 (Organic Chemistry)

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50:64440 Original Reference No. 50:11997f-i,11998a-i,11999a-g
Substituting addition of maleic anhydride to partially hydrogenated naphthalenes and to fluorene. Alder, Kurt; Wollweber, Hartmund; Spanke, Wilhelm (Univ. Cologne, Germany). Ann., 595, 38-54 (Unavailable) 1955. OTHER SOURCES: CASREACT 50:64440.

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 47, 3826f. 1,4-Dihydronaphthalene (I), b₁₁ 86-7°, free from isomers, was prepd. in nearly quant. yield by Hansky's method (U.S. 2,473,997, C.A. 43, 7510g). The addn. of maleic anhydride (II) to I under widely varying conditions showed that, to obtain a stereochemically homogeneous product, a temp. of 120-30° could not be exceeded. I (22 g.) in 20 cc. C₆H₆ heated 9 days at 110-20° with 22 g. II gave over 12 g. (1,2-dihydro-2-naphthyl)succinic anhydride (III), m. 161-2° (from AcOH), unstable toward alk. KMnO₄. The structure of III was detd. unequivocally. I (30 g.) and 40 g. II in 50 cc. C₆H₆ heated 20 hrs. at 190-200° gave about 48 g. of a mixt. (IV) of III and an isomer, m. 140-60°, and 10-12 g. of a resinous still residue. Repeated crystn. of IV from AcOEt gave pure III. On adding III in Me₂CO to a boiling soln. of Na₂CO₃ at such a rate that the Me₂CO distd. regularly during the addn., then cooling, extg. with Et₂O, and acidifying the aq. soln., the free acid, C₁₄H₁₄O₄ (IIIa), sepg. as an oil that crystd. slowly (no m.p. given). III (5 g.) in 200 cc. AcOEt, hydrogenated with PtO₂ as catalyst, gave (1,2,3,4-tetrahydro-2-naphthyl)succinic anhydride (V) (termed "ac-β-tetralylsuccinic anhydride"), m. 163° (giving a m.p. depression when mixed with III); free acid, corresponding to V, m. 159-60° (from AcOEt) (di-Me ester, m. 72°). Dehydrogenation of III with S at 180-230° gave small amts. of C₁₀H₈ and (2-naphthyl)succinic acid, m. 229°. III (7 g.) esterified with CH₂N₂ in MeOH, the soln. evapd., the residue ozonized in AcOEt at -20° to -30°, poured into a small amt. of H₂O contg. H₂O₂, exposed to air several days, dissolved in aq. Na₂CO₃, the soln. extd. with Et₂O, and the aq. layer acidified and reextd. with Et₂O gave 5 g. of an oil, which was decarboxylated by refluxing 2 hrs. with 10 cc. quinoline and 0.8 g. Cu chromite catalyst, adding a 2nd portion of catalyst, cooling, and extg. with Et₂O. This ext., washed with 18% HCl and H₂O, and evapd., gave an oil that was oxidized further by soln. in NaOH and treatment with satd. KMnO₄ soln. until the color persisted, boiled with MeOH, filtered, and the filtrate concd. and acidified, giving BzOH. Thus III could not have been a 1,4-dihydronaphthalene deriv., otherwise the final product would have been o-C₆H₄(CO)₂O. A mixt. of 25 g. 2-tetralone (Cornforth, et al., C.A. 37, 878.9), 25 g. di-Me bromosuccinate, 75 cc. C₆H₆, 10 g. Zn-Hg, and a trace of iodine

stirred and heated on the steam bath, cooled, treated with 200 cc. ice-cold H₂SO₄, extd. with Et₂O, the ext. dried, evapd., freed from tetralone and Me fumarate by distg. at 150°/13 mm., the still residue refluxed 1 hr. in 50 cc. C₆H₆ with 5 g. P₂O₅, treated with 50 cc. H₂O, extd. with Et₂O, the ext. evapd., and the residue sapond. with KOH in MeOH and acidified, gave (3,4-dihydro-2-naphthyl)succinic acid (VI), m. 250° (from AcOH), giving a marked m.p. depression when mixed with either IIIa or (2-naphthyl)succinic acid. VI was unsatd. toward alk. KMnO₄. Its synthesis confirms the structures assigned to III and IIIa. III (10 g.) in 150 cc. PhNO₂ cooled, treated gradually with 9 g. AlCl₃ in 50 cc. PhNO₂, stirred 3 hrs. at room temp., the mixt. decompd. with ice-HCl, extd. with Et₂O, the ext. shaken with satd. aq. NaHCO₃, and the aq. soln. acidified gave almost quantitatively the oxo acid (VIIa), m. 198° (from dil. AcOH). When the mixt. IV was cyclized similarly, the (VIIa) (XII) main product was VIIa, together with smaller amts. of the diastereomer (VIIb), m. 204-5° (from aq. AcOH), of VIIa. A mixt. of VIIa and VIIb gave a sharp m.p. depression. The Me ester of VIIa m. 139°. VIIa (4 g.) reduced by Martin's modification of the Clemmensen reaction (C.A. 30, 6726.1) gave a mixt. which on fractional crystn. from MeCN yielded the less sol. 3-carboxy-4,9-dihydro-5,6-benzindan (VIII), m. 168° (unstable toward KMnO₄), and, from the mother liquors, the 7,8-dihydro deriv. (IX) of VIII, m. 138° (unreactive toward KMnO₄). The original mixt. (4 g.) of VII and IX heated with Pd-C at 280-350° until the loss of CO₂ and H was complete (2 hrs.), the cooled, powd., dark still residue extd. with AcOEt, the ext. evapd., and the residual oil made faintly alk. and steam distd. gave 5,6-benzindan (X), m. 94° (picrate, orange needles, m. 119°). VIIb reduced like VIIa, and the resulting mixt. similarly decarboxylated and dehydrogenated also gave X. I (11.3 g.) and 11 g. (.tplbond.CCO₂Me)₂ in 15 cc. C₆H₆ heated 40 hrs. at 120-30° in a sealed tube, and the product distd. in vacuo gave a brittle still residue and 16.5 g. of an oil b₁₂ 225°, which, sapond. with KOH in MeOH, yielded 60% (2-naphthyl)succinic acid, forming, when boiled with AcCl, the anhydride (XI), m. 134° (from C₆H₆). XI (3 g.) cyclized at room temp. with 4 g. AlCl₃ in PhNO₂, as in the case of III, gave an oxo acid (XII), reduced by the modified Clemmensen method (with xylene in place of PhMe) to 1-carboxy-4,5-benzindan, m. 148° (from dil. AcOH) which was decarboxylated with Cu chromite at 260-70°, to 4,5-benzindan (XIII), colorless liquid (orange-yellow picrate, m. 110°). The anhydride of VI, cyclized with AlCl₃ and PhNO₂ and the product reduced with Zn-Hg and HCl and then dehydrogenated and decarboxylated with Pd-Cu gave XIII. Similarly 10 g. (2-cyclohexen-1-yl)succinic anhydride (C.A. 44, 2925f) was cyclized to an oily oxo carboxylic acid, reduced with Zn-Hg and HCl to an oil which was esterified with CH₂N₂, then heated 3 hrs. with Pd-C at

310-20°, the product extd. with Et2O, the ext. evapd., and the residue sapond., and acidified, giving 1-carboxyindan, identified as the anilide (XIV), m. 140° (cf. Hardy, C.A. 30, 4120.1). Phenylsuccinic anhydride was cyclized with AlCl3 in PhNO2 to 1-carboxy-3-indanone-H2O, m. 84° (120° (after drying in vacuo)) (cf. Speight, et al., C.A. 19, 494), reduced to 1-carboxyindan, forming XIV. Fluorene (XV) (34 g.) and 20 g. II heated 8 hrs. at 220°, freed from residual II by heating in vacuo, the comminuted residue treated with an excess of hot aq. Na2CO3, cooled, filtered, and the filtrate extd. with Et2O to remove XV and acidified gave 27 g. (9-fluorenyl)succinic acid (XVI), needles or small blocks, m. 188° (from MeCN, then AcOEt); di-Me ester, needles, m. 119°. XVI (40 g.) was converted into the anhydride, m. 167° (from AcOEt), by refluxing 3 hrs. with 240 cc. AcCl. The original mixt., without isolating the anhydride, treated with 150 cc. PhNO2, freed from AcCl by distn. in vacuo, **stirred** 4 hrs. at room temp. with 44 g. AlCl3 in 150 cc. PhNO2, poured into a mixt. of 400 g. ice, 400 cc. HCl, and 200 cc. Et2O, shaken vigorously, and allowed to stand a long time gave 13 g. of the cis-XVII (XVIIa), brittle **hexagons**, m. 239° (from MeCN, then AcOEt). The Et2O soln. washed with dil. HCl and H2O and extd. with aq. NaHCO3 gave a ppt. of mixed Na salts which redissolved in more H2O; this soln. treated with C, filtered, and acidified yielded 17 g. of a mixt. of XVIIa and the trans-XVII (XVIIb), which, extd. repeatedly with Et2O, gave pure XVIIb, waxy rhombs or prismatic needles, m. 207° (from MeCN, then AcOEt). The Et2O-insol. residues gave more XVIIa. The yield ratio of XVIIb to XVIIa was 1:2; when the AlCl3-PhNO2 treatment was carried out on the steam bath in lieu of at room temp., this ratio was 1:1. The Me ester of XVIIa, leaflets, m. 125° (from AcOEt ligroine), was formed with MeOH and H2SO4. The Me ester of XVIIb m. 134°. XVIIb (5 g.) underwent a Clemmensen (24 hrs.) reduction with 10 g. amalgamated Zn foil, 30 cc. HCl, 15 cc. H2O, 5 cc. AcOH, and 40 cc. xylene, followed by 2 further addns. of 30 cc. HCl each; the mixt. extd. with C6H6-Et2O (1:1), the washed ext. treated with satd. NaHCO3 soln. and the NaHCO3 soln. acidified gave 4 g. trans-1,2,3,4-tetrahydro-2-carboxyfluoranthene (XVIIIb), needles, m. 166° (from C6H6-ligroine, 1:2); Me ester, m. 98°. Treated similarly with very slight, fully described modifications, XVIIa gave 75% of the cis-isomer (XVIIIa) of XVIIIb, m. 231° (from AcOEt-ligroine); its Me ester, m. 99-100°, refluxed with MeONa in MeOH and acidified gave XVIIIb, m. 166° (whose ester was not isomerized when treated similarly). The Me ester of XVIIIb (1.8 g.) heated 3 hrs. under N at 260-90° with 0.7 g. Pd-C, gave the calcd. amt. of H and about 67% of the calcd. amt. of CO2; the cooled residue extd. repeatedly with AcOEt, the ext. evapd., sapond. with 10% KOH in MeOH, and the mixt. treated with H2O, concd., and extd. with Et2O

yielded 0.5 g. fluoranthene (XIX), m. 110°. The aq. phase when acidified gave 0.7 g. 2-carboxyfluoranthene, yellow needles, m. 219° (from AcOEt-ligroine). Treated similarly, 2.5 g. XVIIIa at 240-320° gave about 84% XIX, but only traces of its 2-carboxy deriv. 18 references.

CC 10 (Organic Chemistry)

L57 ANSWER 13 OF 20 HCA COPYRIGHT 2004 ACS on STN

50:44494 Original Reference No. 50:8580c-i,8581a-i,8582a-e Polynuclear aromatic hydrocarbons. IV. Benzo[c]phenanthrenes. Phillips, Donald D.; Johnson, A. Wm. (Cornell Univ., Ithaca, NY). Journal of the American Chemical Society, 77, 5977-82 (Unavailable) 1955. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 50:44494.

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 50, 4887c. A new method for the prepn. of benzo[c]phenanthrene derivs. has been developed; advantage was taken of the polyfunctional nature of the readily available β -methallylsuccinic anhydride (I) which, when treated with C₆H₆ in the Friedel-Crafts reaction (II), gives rise to the oxo acids Me₂PhCCH₂CH(CO₂H)CH₂Bz (III) and 4,4-dimethyl-1-tetralone-2-acetic acid (IV), both of which may be converted in good over-all yield to the gem-di-Me deriv. 5,5-dimethyl-5,6-dihydrobenzo[c]phenanthrene (V), and thence to 5-methylbenzo[c]phenanthrene (VI). Compds. analogous to V are of interest as potential carcinogenic agents and may prove useful in establishing the role of coplanarity in carcinogenesis among polynuclear aromatic hydrocarbons. Me₂C:CH₂ (134 g.), 100 g. maleic anhydride, and 100 cc. C₆H₆ heated at 180° in a steel bomb, the mixt. kept 4 hrs. at 180°, the excess olefin and C₆H₆ removed at atm. pressure, and the residue distd. in vacuo gave 98.5 g. I, b₉ 137-8°, m. 61-2°; and 8-10 g. γ -methyl- γ -valerolactone-2-acetic acid (VII), b₂ 140-80°, m. 141-2°. I (60 g.) in 200 cc. C₆H₆ added with stirring to 171 g. AlCl₃ in 200 cc. C₆H₆ during 0.5 hr. at 0-5°, the mixt. **stirred** 48 hrs. at room temp. under a stream of N, the mixt. worked up, and the resulting acidic material (47 g.) esterified with MeOH and HCl and distd. gave 5.0 g. unidentified material, b_{1.3} 98-104°, n_D20 1.4980, d₂₁ 1.089 [2,4-dinitrophenylhydrazones, red crystals, m. 149.5-50.5° (from EtOH-EtOAc); it gave sapond. an acid, m. 92-4°]; 16.0 g. Me ester (VIII) of IV, colorless needles, m. 60-1.5° (from aq. EtOH) [2,4-dinitrophenylhydrazones, yellow-orange crystals, m. 159-61° (from EtOH)]; and 7.2 g. Me ester (IX) of III, b_{0.3} 175-8°, n_D20 1.5475. VIII treated with N₂H₄ gave the characteristic dihydropyridazone (X), colorless plates, m. 172.5-3.5° (from EtOH). VIII sapond. gave IV, fine colorless needles, m. 120-1° (from Me₂CO-hexane). IX treated with N₂H₄ gave the corresponding dihydropyridazone, colorless needles; and yielded sapond. II, colorless microcryst.

powder, m. 106.5-8.0° (from Me₂CO-hexane). I (20 g.) in 75 cc. C₆H₆ added with stirring to 67 g. SbCl₅ and 250 cc. C₆H₆ at 0° during 2 hrs., the mixt. **stirred** 18 hrs. at room temp., decompd., washed with acid, extd. with aq. carbonate to give 1.5 g. VII, the C₆H₆ layer evapd., and the brown semisolid residue (13.3 g.) crystd. from aq. EtOH gave α-phenacyl-γ-methyl-γ-valerolactone (XI), colorless plates, m. 69-70°; 2,4-dinitrophenylhydrazone, orange microneedles, m. 226-7° (from EtOAc). XI (4.0 g.) in 75 cc. C₆H₆ treated at 0° with 5.8 g. AlCl₃, and the complex **stirred** at room temp. overnight and worked up in the usual manner gave 0.52 g. unchanged XI and 4.5 g. III, m. 95-100°. III (5.0 g.) in 70 cc. abs. EtOH contg. 1.0 g. 10% Pd. hydrogenated 4 hrs. at 60° and 45 lb. pressure, the mixt. filtered and evapd., and the residue (4.66 g.) treated with p-BrC₆H₄COCH₂Br gave the p-bromophenacyl ester of Me₂PhCCH(CO₂H)₂(CH₂)₂Ph (XII), fine colorless needles, m. 93.5-4.5°. XI (2.0 g.) in 75 cc. abs. EtOH hydrogenated in the same manner, and the resulting oily lactone condensed with C₆H₆ and 2.0 g. AlCl₃ gave 1.4 g. XII. CH₂:CMeCH(CO₂H) (XIII) condensed with ethylene oxide yielded 50% α-(β-methallyl)-γ-butyrolactone (XIV), b_{2.25} 85-7°. XIV treated with ClCH₂CH₂OH yielded α-(2-hydroxyethyl)-γ-methyl-γ-valerolactone, b_{0.6} 118-20°, n_D₂₃ 1.4578. XIV (17.5 g.) in 75 cc. C₆H₆ treated with cooling and stirring with 44.5 g. AlCl₃, the mixt. kept 12 hrs. at room temp. and decompd. in ice and acid, the Et₂O layer extd. with aq. Na₂CO₃, the aq. alk. ext. acidified to give 0.5 g. XII, the Et₂O soln. evapd., and the residual neutral material (13 g.) crystd. from hexane gave α-(2-methyl-2-phenylpropyl)-γ-butyrolactone (XV), **hexagonal** plates, m. 57-8°. XV treated at 80° with excess C₆H₆ and AlCl₃ gave almost 100% XII. XII (8.9 g.) added to 6.96 g. PCl₅, the POCl₃ codistd. with three 15-cc. portions C₆H₆, the crude residue dissolved in 30 cc. dry C₆H₆, the soln. added at 0° during 20 min. to 5.7 g. AlCl₃, the mixt. **stirred** 5 hrs. at 20° and decompd. in the usual manner yielded 7.4 g. oily mixt. (XVI) of 2-(2-methyl-2-phenylpropyl)-1-tetralone and 2-(2-phenylethyl)-4,4-dimethyl-1-tetralone; 2,4-dinitrophenylhydrazone, orange feltlike needles, m. 233-4° (from EtOH-EtOAc). XVI (7.0 g.) in 25 cc. dry Et₂O added at room temp. to 0.48 g. LiAlH₄ in 35 cc. Et₂O, the mixt. refluxed 2 hrs., and decompd. with H₂O and acid, the Et₂O layer evapd., and the residual oil (7.0 g.) crystd. from aq. EtOH gave a mixt. (XVII) of 2-(2-methyl-2-phenylpropyl)- and 2-(2-phenethyl)-4,4-dimethyl-1-tetralol, colorless, needles, m. 94.5°, 99-100°. XVII (1.36 g.) and 0.36 g. P₂O₅ heated 25 min. at 110° and 10 mm., the mixt. dild. with H₂O and extd. with Et₂O, and the ext. chromatographed on Al₂O₃ gave 0.76 g. mixt. (XVIII) of 3-(2-methyl-2-phenylpropyl) and 3-(2-phenethyl)-1,1-dimethyl-1,2-

dihydronaphthalene, colorless oil, n_{D18} 1.5820. XVII (1.5 g.) treated dropwise at room temp. with 2.0 cc. concd. H_2SO_4 , the dark soln. swirled 3 min., poured quickly onto ice and H_2O , and extd. with Et_2O , the ext. washed, dried, and evapd., and the crude residue chromatographed on Al_2O_3 gave 1.2 g. oily 4:1 mixt. of 5,5-dimethyl-5,6,6a,7,8-13-hexahydrobenzo[c] phenanthrene (XIX) and XVIII. An intimate mixt. of 0.51 g. XIX and XVIII heated 4 hrs. at 300° with 70 mg. 10% Pd-C, and the melt chromatographed on Al_2O_3 in hexane yielded 0.33 g. V, colorless fluorescent oil; it developed a color with 2,4,7-trinitrofluorenone (XX). V (0.56 g.) and 0.11 g. 30% Pd-C heated 2 hrs. at 360° , and the melt dissolved in hexane and chromatographed on Al_2O_3 gave 0.30 g. unchanged V and 0.21 g. VI, colorless, fluorescent oil; picrate, orange needles, m. $125-6^\circ$ (from 95% $EtOH$); VI-XX complex, reddish orange needles, m. $151-3^\circ$ (from $AcOH$). I (10 g.) in 50 cc. 6N HCl heated to soln. during 10 min. and then cooled deposited 7.8 g. VII, colorless crystals, m. $137-40^\circ$ (recrystd. from C_6H_6 , m. $141-3^\circ$). VII (15 g.) in 17 cc. C_6H_6 treated with stirring during 0.5 hr. with 29 g. $AlCl_3$, and the mixt. warmed to about 50° , **stirred** 7 hrs. at room temp., and worked up in the usual manner gave 19.7 g. $Me_2PhCCH_2CH(CO_2H)CH_2CO_2H$ (XXI), microcryst. powder, m. $142-4^\circ$. XXI (10 g.) and 10.2 g. Ac_2O refluxed 1 hr., the excess Ac_2O and $AcOH$ distd. in vacuo, the crude anhydride dissolved in C_6H_6 , the soln. treated at 0° with 11.2 g. $AlCl_3$ during 0.5 hr., and the complex decompd. in the usual manner yielded 7.9 g. IV, m. $113-16^\circ$ (recrystd. from Me_2CO -hexane), m. $120-2^\circ$. $NaOEt$ (from 0.15 mole Na) and 8.9 g. HCO_2Et in 150 cc. cold dry Et_2O treated with stirring at 0° with 17.4 g. 4,4-dimethyl-1-tetralone, the red soln. **stirred** 3 hrs. at room temp. and dild. with H_2O and ice, the Et_2O evapd. to give 6.3 g. unchanged tetralone, and the aq. layer worked up gave 8.2 g. formyl deriv. (XXII), b $_4$ $139.5-40^\circ$, n_{D25} 1.6020. XXII (5.0 g.) treated in the cold with stirring with 2.4 g. dry $NaOEt$ in 100 cc. dry C_6H_6 , the mixt. **stirred** 1 hr. at 25° , treated with 7.0 g. $BrCH_2CO_2Et$ in 15 cc. C_6H_6 , **stirred** 2 hrs. at 25° , refluxed 20 hrs., and dild. with H_2O , the excess solvent removed, the residual crude oil refluxed 4 hrs. with 100 cc. 10% aq. $NaOH$, and the mixt. acidified gave 2.7 g. alkylated formyl deriv. and 1.4 g. IV, colorless microneedles, m. $120-1^\circ$. VIII (10.0 g.) in 100 cc. dry Et_2O treated during 1 hr. with 0.04 mole $PhMgBr$ in 50 cc. Et_2O , and the soln. refluxed 45 min. and decompd. in the usual manner yielded 8.8 g. lactone XXIII, m. $147-50^\circ$ (probably contg. the corresponding hydroxy ester); the crude XXIII subjected to a Clemmensen reduction during 26 hrs. gave 4.3 g. unchanged XXIII and 3.2 g. 1-phenyl-4,4-dimethyl-1,2,3,4-tetrahydronaphthalene-2-acetic acid (XXIV), colorless oil. XXIV cyclized as described for XVI yielded 78% 5,5-dimethyl-8-oxo-

5,6,6a,7,8,13-hexahydrobenzo[c]phenanthrene, oil;
2,4-dinitrophenylhydrazone, orange felt-like needles, m.
235-6° (from EtOAc); the ketone hydrogenated catalytically
gave 65% pure XIX. IV (2.5 g.) in 50 cc. 1:1 aq. MeOH neutralized
with NaOH, the mixt. treated with 0.14 g. NaBH₄, and the soln.
heated 10 min. to 60°, and decompd. with aq. acid yielded 2.4
g. 4,4-dimethyl-1-hydroxy-1,2,3,4-tetrahydronaphthalene-2-acetic
acid (XXV), colorless needles, m. 154-5°. XXV (5.2 g.) in 30
cc. C₆H₆ added to 1.85 g. P205 in 20 cc. refluxing C₆H₆,
the mixt. refluxed 2 hrs., decompd. with H₂O and extd. with H₂O, the
resulting oil (3.8 g.) refluxed with 30 cc. dil. HCl, the crude
product (3.6 g.) from the hydrolysis dissolved in 75 cc. dry C₆H₆,
the soln. treated with stirring with 3.3 g. AlCl₃ at 0°, and
the complex **stirred** 4 hrs. at room temp. and worked up in
the usual manner gave 2.6 g. XXIV. I (30.6 g.) in 125 cc. dry Et₂O
treated at -70° during 2 hrs. with 0.02 mole PhMgBr in 75 cc.
dry Et₂O, and the mixt. **stirred** 3 hrs. at -70° and
decompd. with satd. aq. NH₄Cl yielded 14.6 g. unchanged I and 11 g.
CH₂:CMeCH₂CH(CO₂H)CH₂Bz (XXVI); XXVI (7.6 g.) treated with CH₂N₂
gave 4.75 g. Me ester (XXVII), colorless oil, b_{1.3} 147-9°,
n_D²² 1.5188; 2,4-dinitrophenylhydrazone, yellow-orange needles, m.
113-14°. XXVII sapond. and lactonized gave XI; it gave
alkylated with C₆H₆ and then sapond. III in good yield. The
ultraviolet absorption spectra of VI and the 5,6-dihydro deriv. of I
are recorded.

CC 10 (Organic Chemistry)

L57 ANSWER 14 OF 20 HCA COPYRIGHT 2004 ACS on STN

50:20145 Original Reference No. 50:4189b-i,4190a-i Triterpenoids.
XLIII. Constitution of compounds obtained by the dehydration of
 α -amyrin and related alcohols. Allan, G. G.; Spring, F. S.;
Stevenson, Robert; Strachan, W. S. (Roy. Tech. Coll., Glasgow, UK).
Journal of the Chemical Society, Abstracts 3371-7 (Unavailable)
1955. CODEN: JCSAAZ. ISSN: 0590-9791.

GI For diagram(s), see printed CA Issue.

AB As a basis for a more systematic nomenclature of the dehydrogenation
products here described, the hydrocarbon C₂₇H₄₆ (A), having the
constitution and stereochemistry represented is called novursane.
In the detn. of the constitution of a no. of products obtained by
the dehydration of α -amyrin (I) and related compds. the
treatment of 3 β -hydroxyurs-12-en-11-one (II) with PCl₅ gave 60%
8,10,14-trimethyl-5 ξ -novursa-3(4),12-dien-11-one (III)
("α-amyradienone-I"), m. 197-9°, [α]_D 167°
(c 2.9), and 10% 8,10,14-trimethylnovursa-3(5),12-dien-11-one (IV)
("α-amyradienone-II"), m. 155-6°, [α]_D
147° (c 0.8). IV (0.3 g.) was also formed by refluxing 0.5
g. III in 50 cc. AcOH contg. 5 cc. concd. HCl 16 hrs. with addn. of
2 cc. concd. HCl every 4 hrs. A mixt. of 800 mg. III and NaOMe

(from 1 g. Na) in 15 cc. MeOH and 5 cc. 100% H₂NNH₂.H₂O was autoclaved at 200° 15 hrs., the product taken up in 100 cc. petr. ether, chromatographed on Al₂O₃, eluted with petr. ether and crystd. from MeOH to yield 310 mg. prisms of 8,10,14-trimethyl-5ξ-novaursa-3(4),12-diene (V), m. 134-5°, [α]_D 109° (c 1.3), identical with "d-α-amyradiene" (Vesterberg and Westerlind, C.A. 16, 3642), obtained by PCl₅, dehydration of I. V (1.0 g.) in 200 cc. CHCl₃ was treated with 2 moles O₃ at -35°, the mixt. **stirred** at room temp. with 3 g. Zn dust and 50 cc. AcOH 1 hr., the filtered soln. washed with five 250-cc. portions H₂O, the CHCl₃ evapd. and the residue crystd. from MeOH. Fractional crystn. from MeOH yielded 350 mg. product, which, chromatographed on Al₂O₃, eluted with petr. ether and recrystd. from MeOH, yielded 250 mg. needles of VI, C₂₇H₄₂O, m. 146-8°, [α]_D 210°, unchanged after 2.5 hrs. refluxing with 5% KOH in EtOH. Further elution with petr. ether-benzene (2:1) and crystn. from MeOH gave a small amt. of VII, C₂₇H₄₂O₂, m. 204-6°, [α]_D 184°. Distn. of the H₂O washings yielded acetone, identified as the dinitrophenylhydrazone, m. 121-4°. Treatment of 700 mg. V in 7 cc. CHCl₃ with 700 mg. Cl₃CCO₂H at room temp. for 1 hr. and recrystn. from acetone gave 200 mg. **hexagonal** prisms of 8,10,14-trimethylnovursa-3(5),12-diene (VIII), m. 70-2°, [α]_D 123° (c 1.4), λ 2080 Å. (ε 4500). VIII was also formed by the Wolff-Kishner reduction of IV by which its structure is established. The infrared absorption spectrum of VI includes a strong band at 1740 cm. ⁻¹ (in CCl₄) and, consequently, VI contains a CO group in a 5-membered ring. It also gives a yellow color with C(NO₂)₄ and is recovered unchanged after treatment with alkali, suggesting that the rings A and B are fused in the more stable form. The change in [M]_D (+450°) accompanying the conversion of I into VI is in agreement with values observed for comparable reactions, proving that the ring fusion is cis-β. Treatment of II with HI in AcOH (Ewen, et al., C.A. 38, 2028.4) gave 5,8,14-trimethylnovursa-9(10),12-dien-11-one (IX), m. 170-1°, [α]_D 171° (c 3.3), λ 2040, 2580, 2900 Å. (ε 9900, 11,000, 10,200), yellow color with C(NO₂)₄. The ultraviolet absorption spectrum of IX ("α-amyradienone-III") closely resembles that of 12-oxooleana-9(11),13(18)-dien-3β-yl acetate (X) and 12-oxoursa-9(11),13(18)-dien-3β-yl acetate (XI), the characteristic absorption spectra of which have been related to the geometry of the C:CC-(O)C:C chromophore. The constitution thus assigned to IX is confirmed by its formation from IV. IV (2 g.) in 10 cc. glacial AcOH was treated with 5 cc. HI (d. 1.7) and refluxed for 8 hrs. Crystn. from MeOH gave 1.2 g. laminas of IX. Wolff-Kishner reduction or refluxing with LiAlH₄ in Et₂O converted IX into 5,8,14-trimethylnovursa-9(10),12-diene (XII), m. 98-9°, [α]_D 120° (c 2.8), λ 2080 Å.

(ϵ 13,200), orange color with $C(NO_2)_4$. This behavior of IX is similar to that of X. Catalytic hydrogenation of 600 mg. IX in 100 cc. AcOH in the presence of Pt (from 250 mg. PtO_2) 24 hrs. and crystn. of the reduction product from acetone-MeOH gave 350 mg. plates of 5,8,14-trimethyl-9 ξ ,10 ξ -novurs-12-ene (XIII), m. 95-6°, $[\alpha]_D^{140}$ (c 1.4), λ 2060 A. (ϵ 2750), yellow color with $C(NO_2)_4$. IX differs from X and XI in its reduction to the monoethylenic hydrocarbon XIII whereas X and XI undergo catalytic hydrogenolysis to the corresponding nonconjugated diene. XII (150 mg.) in 5 cc. $CHCl_3$ and 50 cc. AcOH contg. 10 cc. concd. HCl was refluxed 16 hrs. with the addn. of 2 cc. concd. HCl every 2 hrs. Crystn. of the product from $CHCl_3$ -MeOH gave 50 mg. "1- α -amyradiene" (C.A. 38, 2028.4), m. 193-4°, $[\alpha]_D^{-110}$ (c 1.9), λ 2360, 2410, 2500 A. (ϵ 13,200, 14,500, 8550), also prepd. from V by treatment with BF_3 in AcOH and previously by V. and W. (loc. cit.) by dehydration of I with **P2O5**. According to Ewen, et al. (C.A. 38, 2028.4), dehydration of urs-9(11),12-dien-3 β -ol (XIIIa) with PCl_5 gives a dichloro- α -amyradiene, which with Zn yields "d- α -amyratriene" (XIV) whose ultraviolet absorption spectrum shows that the new unsatd. bond is remote from the conjugated system in ring C. XIIIa (3.0 g.) in 80 cc. petr. ether (b. 60-80°) was shaken with 1.47 g. PCl_5 1.5 hrs. and refluxed 2 min. Crystn. of the product from MeOH- $CHCl_3$ gave XIV, m. 132-4°, $[\alpha]_D^{439}$ (c 0.9), λ 2780 A. (ϵ 9500). The constitution of XIV was established by its formation from III. III (500 mg.) in 200 cc. Et_2O was refluxed with 500 mg. $LiAlH_4$ 3 hrs., the crude product in 50 cc. pyridine was refluxed 15 hrs. with 20 cc. $POCl_3$, and the product crystd. from MeOH produced 200 mg. needles of XIV, 8,10,14-trimethyl-5 ξ -novursa-3(4),9(11),12-triene. IX (1.0 g.) in 200 cc. anhyd. Et_2O was kept at 0° in the presence of $LiAlH_4$ 72 hrs., and the product isolated in the absence of traces of mineral acid and crystd. from MeOH to yield 5,8,14-trimethylnovursa-1(10),9(11),12-triene (XV), m. 145-6°, $[\alpha]_D^{-358}$ (c 1.6), λ 3200 A. (ϵ 15,000), similar optically to ergosta-5,7,14,22-tetraen-3 β -yl acetate. Treatment of XV with HCl in AcOH and crystn. from MeOH gave needles of 5,8,14-trimethylnovursa-9(10),11,13(18)-triene (XVI), m. 140-2°, $[\alpha]_D^{-450}$ (c 0.5), λ 2860, 2950, 3080 A. (ϵ 28,200, 33,800, 24,500), previously obtained by dehydration of XIIIa by **P2O5**. Ergosta-4,6,8(14),22-tetraene, which contains a chromophore comparable with that in XVI, has similar absorption. The calcd. value (2940 A.) for the position of the absorption max. in XVI, on the basis of Woodward's empirical rules, is in excellent agreement with the observed value.

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49:32158 Original Reference No. 49:6126h-i,6127a-i,6128a-h Preparation and properties of 3,5-di-O-benzoyl-1,2-O-(α -hydroxybenzylidene)- α -D-ribose, and the orthobenzoic acid derivative of D-ribofuranose. Ness, Robert K.; Fletcher, Hewitt G., Jr. (Natl. Inst. of Health, Bethesda, MD). Journal of the American Chemical Society, 76, 1663-7 (Unavailable) 1954. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 49:32158.
- AB The hydrolysis of tri-O-benzoyl- β -D-ribofuranosyl bromide (I) gave the previously reported 2,3,5-tri-O-benzoyl- β -D-ribose (II) (cf. C.A. 49, 3024f), together with a new, cryst. isomer (III). III, which is stable to dil. acids, is readily isomerized by aq. pyridine to II. The synthesis of III through the hydrogenolysis of amorphous 3,5-di-O-benzoyl-1,2-O-(α -benzyloxybenzylidene)- α -D-ribose (IV) indicates that it is most probably 3,5-di-O-benzoyl-1,2-O-(α -hydroxybenzylidene)- α -D-ribose (V). III with HBr afforded a cryst., highly reactive 3,5-di-O-benzoyl-D-ribofuranosyl bromide (VI) which on hydrolysis gave amorphous 3,5-di-O-benzoyl-D-ribose (VII). The successive oxidation, reduction, deacetylation, and benzylation of VII led to erythritol tetrabenzoate (VIII). The treatment of either III or VI with ZnCl_2 in Ac_2O gave a cryst. 1,2-di-O-acetyl-3,5-di-O-benzoyl-D-ribose (IX). With HBr IX gave an amorphous bromide yielding on hydrolysis a cryst. substance which appeared to be 3,5-di-O-benzoyl-1,2-O-(α -hydroxyethylidene)- α -D-ribose (X), an orthoacetic acid deriv. Ortho acid derivs., a relatively rare type of substance, are briefly discussed. II (10.11 g.) in 30 cc. CH_2Cl_2 and 3.5 cc. Ac_2O treated with 10 cc. 32% HBr in glacial AcOH , the mixt. allowed to stand 6 min. at 20° , poured into a mixt. of ice water and CH_2Cl_2 , the org. layer quickly washed with cold aq. NaHCO_3 , dried with Na_2SO_4 , filtered through C, concd. in vacuo at about 35° , the resulting crude frothy mass dissolved in 40 cc. Me_2CO and 2 cc. H_2O , the soln. let stand 75 min. at room temp., treated with CH_2Cl_2 , the mixt. washed with cold. aq. NaHCO_3 , dried with Na_2SO_4 , evapd. in vacuo at 30° , and the semicryst. residue treated with 70 cc. Et_2O and 35 cc. pentane yielded 5.10 g. (50%) practically pure V, m. $142-3^\circ$, $[\alpha]_D^{25} 86^\circ$ (c 0.93, CHCl_3), recrystg. from 2:1 $\text{Me}_2\text{CO}-\text{H}_2\text{O}$ in fine needles, m. $142-3^\circ$, $[\alpha]_D^{25} 85.3^\circ$ (c 0.97, CHCl_3); the mother liquor concd. and the resulting sirup recrystd. from Et_2O -pentane yielded 32% crude II. Pure D-ribose (5 g.) converted successively to Me D-ribofuranoside, its tribenzoate, and 2,3,5-tri-O-benzoyl- β -D-ribofuranosyl bromide as described previously (loc. cit.), the amorphous bromide dissolved in 60 cc. Me_2CO and 3 cc. H_2O , the soln. allowed to stand 40 min. at room temp., dild. with CH_2Cl_2 , washed with cold aq. NaHCO_3 , dried, evapd., and the residual sirup crystd. from 120 cc. Et_2O and 60 cc. pentane gave 6.55 g. (43%) V, m. $141-2^\circ$; the mother liquor concd., the resulting sirup

dissolved in 60 cc. pyridine and 37 cc. H₂O, and the soln. cooled to -5° gave II-pyridine addn. compd., which, dried in vacuo over H₂SO₄, yielded 5.4 g. II (total yield 78%). II (5.00 g.) in 25 cc. (CH₂Cl)₂ over solid Drierite nearly satd. with gaseous HBr, the mixt. kept 65 min. at 0°, filtered, concd. in vacuo at room temp., the resulting thick sirup dissolved in 10 cc. (CH₂Cl)₂ and 5 cc. quinoline, the soln. cooled, treated with 2.5 cc. PhCH₂OH, allowed to stand 19 hrs. at 0-5°, the mixt. dild. with CH₂Cl₂, poured on ice, and the org. layer washed with cold 3N H₂SO₄ and aq. NaHCO₃, dried with Na₂SO₄, and concd. in vacuo, gave 6.5 g. sirupy residue; a sample of the residue showed $[\alpha]_D^{81}$ (c 4, 49, Ph CH₂OH); with 1 drop HBr in PhCH₂OH the rotation fell to 22° in 2 hrs. [the rotation of benzyl β -D-ribofuranoside tribenzoate is $0.0 \pm 0.5^\circ$ (l 0.5 dm., PhCH₂OH)]; the remainder of the sirup (6.46 g.) dissolved in 40 cc. EtOAc, hydrogenated 3 hrs. at room temp. over 5 g. prereduced Pd-C, the mixt. filtered, concd., and the residual sirup crystd. from 25 cc. dry Et₂O gave 1.07 g. (21%) V, m. 141-3°; the material isolated from the mother liquor, recrystd. from CCl₄, yielded 2.59 g. (52%) II, m. 103-7°. V (0.5114 g.) in 25 cc. 18:7 dioxane-H₂O showed a specific rotation of 74°; addn. of 0.016 cc. of about 41% HBr did not change this value during 2 months; a similar soln. having asp. rotation of 73° treated with 2 drops NH₄OH changed in 2 hrs. to 66.7°. II showed a rotation of 67.3° in 18:7 dioxane-H₂O (c 1.01); 1.3 hrs. after the addn. of 2 drops concd. NH₄OH it changed to 67.6°. V (1 g.) in 10 cc. pyridine and 2 cc. H₂O kept 31.5 hrs. at room temp., the soln. cooled to 0°, dild. with 6 cc. H₂O, seeded with 2,3,5-tri-O-benzoyl-D-ribose contg. pyridine of crystn., the mixt. treated with 4 cc. H₂O, and the resulting ppt. dried in vacuo at 40° over P₂O₅ gave 0.89 g. product, which, recrystd. from 2 cc. abs. EtOH and 3.6 cc. pentane, yielded 0.65 g. (65%) II, m. 102-4°, recrystg. from 2 parts CCl₄ 0.60 g. fine needles, m. 106-8°, $[\alpha]_D^{68.7}$ (c 2.05, CHCl₃). V (0.5489 g.) in CH₂Cl₂ (total vol. 15.00 cc.) showed a rotation of 4.66° in a 1.5-dm. tube; a gentle stream of HBr passed over the surface of the soln. in the tube for 30 sec., and the soln. mixed showed the following observed rotations: 2.79° (1.5 min.), 4.63° (2.8 min.), 5.32° (5.7 min.), 4.98 (10 min.); the mixt. concd. in vacuo at 0°, and the resulting semicryst. mass recrystd. from 1 cc. dry Et₂O and 1.1 cc. pentane at 0° gave 0.497 g. (99%) VI, m. 88-91° (decompn.); recrystd. from 11 cc. 3:5:3 CH₂Cl₂Et₂O-pentane at -5°, the product (0.260 g.) 104-5° (decompn.), $[\alpha]_D^{96}$ (3 min.), mutarotating to 27° (60 min.) (c 0.47, abs. EtOH). VI (1.00 g.) **stirred** 40 min. in a cooled mixt. of 10 cc. Me₂CO, 1 cc. H₂O, and 1 g. AgCO₃, the mixt. filtered, and the filtrate dried with Na₂SO₄ and concd. in vacuo at 25°, gave a

colorless clear sirup which failed to crystallize; a sample (0.3840 g.) in a little glacial AcOH treated with 50.0 cc. 0.0568N Pb(OAc)₄ in glacial AcOH and the mixt. dild. to 100 cc. with glacial AcOH and analyzed after 1, 4, and 22 hrs. by the method of Hockett and McClenahan (C.A. 33, 6803.4) showed the consumption of 0.78 mole oxidant/mole compd.; the remainder of the oxidation mixt. (39.5 cc.) poured into a cold mixt. of 200 cc. CH₂Cl₂, 200 cc. H₂O, 40 g. NaOAc, 2.3 g. KI, and 6 cc. 0.1N aq. Na₂S₂O₃, thoroughly shaken, the org. layer washed with aq. NaHCO₃, dried with Na₂SO₄, concd. in vacuo, the residual sirup dissolved in 8 cc. abs. EtOH, hydrogenated 19 hrs. at 2250 lb. pressure over Raney Ni, the mixt. filtered, the filtrate concd. in vacuo, the residual sirup deacylated in the usual manner with Ba(OMe)₂, and the product treated with BzCl in pyridine, worked up in the usual way, and crystd. from Et₂O yielded 0.0926 g. (41%) crude VIII, m. 181-6°, which, recrystd. from 1:1 C₆H₆hexane and then from 1:1 CH₂Cl₂-abs. EtOH, showed no rotation in CHCl₃ (c 1.65, 4 dm.) and m. 189-90°. Fused ZnCl₂ (0.45 g.) in 8 cc. Ac₂O treated with cooling during 6 min. with 1.0 g. II in portions, the mixt. allowed to stand 20 hrs. at 5° poured into 60 cc. H₂O, the pptd. brittle mass dissolved after several hrs. in 3 cc. warm abs. EtOH, and the soln. cooled gave 0.52 g. (54%) IX, sheaves of heavy needles, m. 125-7°, [α]_D -3.2° (c 1.49, CHCl₃), which, recrystd. from 11 parts abs. EtOH, yielded pure IX, m. 127-8°, [α] -3° (c 0.82, CHCl₃). VI (0.1024 g.) in 2.00 cc. Ac₂O (observed in a 0.5-dm. tube) mutarotated rapidly [0.53° (2.0 min.), 0.91° (3 min.), 1.12° (5.4 and 13.6 min.)]; the soln. treated after 15 min. with a small amt. of powd. fused ZnCl₂ gave an almost instant change of the rotation to 0.31° (1.5 and 5.3 min.); the mixt. poured after 9 min. on ice and the ppt. recrystd. from 0.5 cc. abs. EtOH gave 0.0642 g. (60%) IX, m. 126-7°. II (1.03 g.) in 5 cc. CH₂Cl₂ and 0.3 cc. Ac₂O treated with 7 cc. 32% HBr in glacial AcOH, the mixt. poured after 16 min. into ice and CH₂Cl₂, the org. layer washed with H₂O and aq. NaHCO₃, dried with Na₂SO₄, concd. in vacuo at 30°, and the residual clear sirup crystd. from 5 cc. dry Et₂O and about 2.5 cc. pentane gave 0.132 g. (15%) crude X, m. 92-7°, recrystd. twice from 10 cc. warm Et₂O, m. 129-30°, [α]_D 66.4° (c 1.26). X (0.1217 g.) in 7.2 cc. dioxane dild. to 10.0 cc. with H₂O showed in a 1.5-dm. tube at 20° a rotation of 1.13°; 1 drop 41% HBr added changed it in 16 hrs. to 1.03°; with 0.15 cc. added pyridine it changed more rapidly: 0.99° (3 min.), 0.79° (7 hrs.), 0.48° (24 hrs.), 0.40° (31 hrs.), 0.32° (48 hrs., const.). IX (1.00 g.) in 10.0 cc. (CH₂Cl)₂ showed a rotation of -0.37° in a 1.5-dm. tube; 0.24 cc. added Ac₂O changed it to -0.36°; with 9.7 cc. 32% HBr in glacial AcOH the following rotations were observed: -1.40° (1.0 min.), -0.05° (1.4 min.), 1.21° (3.5 min.), 1.24° (12

min.). The mixt. poured after 18 min. into ice water and CH_2Cl_2 , the org. layer washed with aq. NaHCO_3 and H_2O , dried with Na_2SO_4 , concd. in vacuo at 35° , and the resulting thick sirup recrystd. from 2 cc. Et_2O gave 0.188 g. crude X, m. $115-18^\circ$; a 2nd crop of 0.063 g., m. $115-19^\circ$, raised the yield to 28%; the crude X recrystd. from 1:1:1 CH_2Cl_2 - Et_2O -pentane and then from 2:1 Et_2O -pentane yielded 0.084 g. pure X, needles, m. $127-8^\circ$, $[\alpha]_D^{25} 68.2^\circ$ (c 0.33, CHCl_3); recrystd. again from Et_2O , m. $128-9^\circ$; a 2nd recrystn. from CH_2Cl_2 -pentane gave a product which showed a double m.p. at $105-6^\circ$ and $127-8^\circ$. Pure β -D-ribofuranose tetrabenzoate (0.4175 g.) in 4.0 cc. Ac_2O treated at 20° with 1 cc. of a soln. of 2.0 g. fused ZnCl_2 in 10 cc. Ac_2O , the mixt. poured on ice after the mutarotation ceased (4 hrs.), and the ppt. gum crystd. from abs. EtOH gave 0.2084 g. (56%) 1-O-acetyl-2,3,5-tri-O-benzoyl-D-ribose, m. $128-9^\circ$, recrystg. from 5 cc. abs. EtOH in **hexagonal** micaceous plates, m. $129-30^\circ$.

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49:1254 Original Reference No. 49:268i,269a-i,270a-i,271a-i,272a-i,273a-i,274a-i,275a-f Terramycin. X. The structure of Terramycin. Hochstein, F. A.; Stephens, C. R.; Conover, L. H.; Regna, P. P.; Pasternack, R.; Gordon, P. N.; Pilgrim, F. J.; Brunings, K. J.; Woodward, R. B. (Harvard Univ.). Journal of the American Chemical Society, 75, 5455-75 (Unavailable) 1953. CODEN: JACSAT. ISSN: 0002-7863.

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 48, 10712b. The antibiotic Terramycin (I) has been shown to have the structure II; the stereochem. assignments in this structural formula are tentative. Anhyd. II was recrystd. twice from PhMe, the resulting purified material (1.8 g.) dissolved in 2 l. dry PhMe, the soln. refluxed 2 h. through a Soxhlet extractor charged with CaH_2 , the hot soln. filtered and cooled, and the cryst. deposit dried to const. wt. at $100^\circ/0.1$ mm. to give pure I (4-dimethylamino-1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,10,12,12a-hexahydroxy-6-methyl-1,11-dioxo-2-naphthacenecarboxamide), pale yellow crystals, m. $184.5-5.5^\circ$ (decompn.) (placed in a bath at 175° and heated at $2^\circ/\text{min.}$), $[\alpha]_D^{25} -197^\circ$ at equil. (0.1N HCl); gave pos. FeCl_3 , Pauly, Friedel-Crafts, Fehling, and Molisch tests; contained 7.8 mol active H/mol; λ_{max} 245 (4.20), 357 (4.10) in HCl-EtOH , 245 (4.20), 266 (4.14), 380 μ (log ϵ 4.16) in EtOH-NaOH ; acid consts. of I hydrochloride 3.49, 7.55, 9.24 in H_2O ; the apparent pK_a of I shifts to 8.0 and 9.8 in 1:1 HCONMe_2 - H_2O . I in Me_2CO or H_2O was oxidized by several moles KMnO_4 , but yielded no readily identified products other than NH_3 and Et_2NH . I.HCl in H_2O consumed 8 equivs. HI_2O_4 within 2 h. at 25° ; the hypiodite oxidn. of I

yielded 1.75 equivs. CHI_3 ; the oxidn. of I in hot 15% HNO_3 yielded 1.3 equivs. $(\text{CO}_2\text{H})_2$, and smaller amts. of an unidentified nitrated phenolic acid, m. $217.5-18.5^\circ$. CH_2N_2 (6 g.) in 300 cc. dry Et₂O added to 18.6 g. anhyd. I in 400 cc. dry dioxane at 10° , the soln. let stand 1.5 h. and dild. with 1400 cc. com. hexane, the amorphous ppt. (16.9 g.) dried in vacuo and **stirred** 0.5 h. with 100 cc. MeOH, and the resulting cryst. ppt. recrystd. from 50% aq. MeOH yielded 2.0 g. (10%) dimethylterramycin (III), decomp. without melting at 225° , insol. in H_2O , pyridine, and the common org. solvents, λ_{max} . 272 (4.40), 352 $\text{m}\mu$ (log ϵ 4.0). III dissolved in HCl in MeOH, the soln. dild. with Et₂O, and the ppt. carefully recrystd. from EtOAc-MeOH contg. HCl gave III.HCl, yellow **hexagonal** plates, decompd. without melting at 175° , $[\alpha]_{\text{D}28} -110^\circ$ (MeOH); pKa 7.7 in aq. HCONMe₂. An amorphous unstable material which evolved Me₃N on mild alkali treatment was obtained in 70% yield in the prepn. of III. Anhyd. I (10 g.) in 200 cc. dry dioxane made up with Ac₂O to 1 l., the mixt. let stand 14 days at $25-30^\circ$, evapd. to dryness in vacuo below 35° , and the cryst. residue recrystd. twice from PhMe yielded 8.8 g. (75%) 5,12a-di-Ac deriv. of I, m. $208-13^\circ$ (decompn.), $[\alpha]_{\text{D}25} 211^\circ$ (Me₂CO); pKa 6.75 and 8.85 in aq. HCONMe₂; gave treated 5 min. at 25° with N NaOH I. I.HCl (2.5 g.) in 7 cc. pyridine treated at 5° with 3.6 g. PhSO₂Cl, the mixt. let stand overnight at 5° and poured into 50 cc. Et₂O, the gummy ppt. **stirred** 1 h. with 25 cc. H_2O , and the resulting light tan cryst. solid recrystd. twice from HCONMe₂, washed with Me₂CO, and dried 3 h. in vacuo at 100° gave benzenesulfonylterramycinonitrile (10-benzenesulfonyloxy-4-dimethylamino-1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,12,12a-pentahydroxy-6-methyl-1,11-dioxo-2-naphthacenitrile) (IV) contg. 1 mol HCONMe₂, m. $210-11^\circ$; pKa 6.95; $[\alpha]_{\text{D}25} -378^\circ$ (HCONMe₂); λ_{max} . 275 (4.23), 342 $\text{m}\mu$ (log ϵ 4.06) in acid MeOH; this with Ac₂O-pyridine gave a solid which was recrystd. from EtOH to yield a triacetate crystg. with 0.5 mol H_2O and 0.5 mol EtOH, $[\alpha]_{\text{D}25} 8^\circ$ (HCONMe₂), pKa 5.3. Terranaphthol (3-hydroxymethyl-4-methyl-1,8-naphthalenediol) (V) was prepd. as previously described (C.A. 48, 2020d) and purified through the triacetate, m. $148.7-9.4^\circ$, to give pure V, m. $172.4-3.0^\circ$; it gave a green color with alc. or aq. FeCl_3 and a red ppt. with aminoantipyrine; λ_{max} . 232 (4.79), 312-341 $\text{m}\mu$ (log ϵ 3.89); pKa 7.5; it gave with peroxide, HNO_3 , or $\text{K}_2\text{Cr}_2\text{O}_7$ in AcOH intractable tars and was not attacked by Ag₂O in Et₂O. V in dioxane added to 5 mol CH_2N_2 in Et₂O, and the mixt. let stand overnight at 25° gave a mono-Me ether, b.p. 160° , which crystd. slowly from C₆H₆-ligroine and from Et₂O-ligroine to give 25% solid product, m. $88-91^\circ$. V (40.8 mg.) in 2 cc. abs. EtOH added to 5 cc. 0.5M aq. H_3BO_3 , showed pH 2.20, whereas the blank from 5 cc. H_3BO_3 and 2 cc. EtOH had pH 5.00;

the change in the pH is partly caused by the natural acidity of the added V. V (0.2 g.) ground in a mortar with 2 g. NaOH and 2 g. KOH, the mixt. heated in a Ni crucible 15 min. at 260-70°, the brown melt cooled, dissolved in 15 cc. H₂O, quickly acidified with cooling with 4N H₂SO₄ to pH 1, and dild. to 30 cc., and the insol. crystals and tar filtered off, dried, and recrystd. 3 times with C from hot H₂O and from aq. MeOH yielded 0.06 g. terranaphthoic acid (1,8-dihydroxy-4-methyl-3-naphthoic acid (VI), yellow tan crystals, m. 233-5° with some decompn. above 220° when placed in a bath at 200° and heated at 2°/min.; pKa 5.5 and 7.8; λ_{\max} . 3.2, 5.85 μ ; λ_{\max} . 236 (4.60), 310 (3.76), 343 m μ (log ϵ 3.71); gave a red aminoantipyrine test and a green color with aq. or alc. FeCl₃; gave on decarboxylation in boiling quinoline with Cu bronze catalyst 0.35 mol CO₂. VI (0.05 g.) in 0.5 cc. dioxane and 0.5 cc. Et₂O treated at 0° with 0.05 g. CH₂N₂ in 10 cc. Et₂O, the mixt. let stand overnight at room temp., and the resulting oily product sublimed and crystd. 3 times from MeOH gave the Me ether Me ester of V, pale yellow needles, m. 101-2° (dried at 80°/0.1 mm.), insol. in aq. NaHCO₃, did not give a color with FeCl₃; λ_{\max} . 3.0, 5.83 μ . 1,8-Dihydroxy-2-naphthaldehyde (VII), m. 137.8-8.5°, was obtained in 6% yield by the method of Morgan and Vining (C.A. 15, 1503) and purified by extn. with cyclohexane in a Soxhlet app., recrystn. from cyclohexane, and sublimation at 135°/0.1 mm.; pKa 4.5; λ_{\max} . 2.9, 6.15 μ ; λ_{\max} . 265 (4.53), 324 (3.50), 420 m μ (log ϵ 4.00). VII (0.15 g.) fused 3 min. at 220° with 0.7 g. NaOH and 0.7 g. KOH, the melt dissolved in H₂O, cooled, acidified, the amorphous ppt. filtered off, recrystd. from aq. EtOH and twice from PhMe yielded 40 mg. 1,8,2-(HO)₂C₁₀H₅CO₂H, colorless crystals, m. 170.5-1.5 with vigorous gassing; pKa 3.2 and above 12; λ_{\max} . 6.05 μ in dioxane; λ_{\max} . 245 (4.72), 314 (3.67), 360 (3.94), 372 m μ (log ϵ 3.91); was decarboxylated in excellent yield to 1,8-C₁₀H₆(OH)₂ when heated to 125°/0.05 mm. Alkali fusion of 4,5,1-(HO)₂C₁₀H₆CHO gave 1,8,4-(HO)₂C₁₀H₅CO₂H, m. 58-60° (decompn.); pKa 5.6 and 8.2; it underwent rapid decarboxylation in vacuo at 130°; λ_{\max} . 220 (4.44), 335 m μ (log ϵ 4.00). Zn dust washed with 0.1N HCl and then with EtOH, dried at 25° in vacuo, heated 15 min. in a slow H stream at 300°, and cooled under H gave purified Zn dust. V (100 mg.) mixed with 5 g. purified Zn dust, the mixt. heated in a Pyrex tube in a slow stream of N to near the softening point of the glass, and the alkali-insol. viscous green oil condensing in the cooled parts of the tube distd. gave 7.8 mg. (10%) 1,3-C₁₀H₆Me₂, b0.1 80°, m. -10 to -8°; picrate, m. 116.5-18.5°; styphnate, m. 118-20°; C₆H₃(NO₂)₃ adduct, m. 134-6°. VI (75 g.) mixed with 7.5 g. purified Zn dust, the mixt. heated in a H stream, the crude product (18 mg.) dissolved in 0.5 cc. CS₂, and the soln.

washed with 10% aq. NaOH and distd. gave a mixt. contg. about 70% 1-C10H7Me (VIII) and lesser quantities 2-C10H7Me (IX) and C10H8. VIII distd. similarly with Zn dust gave small amts. of IX and C10H8, while IX yielded only traces of C10H8. The NaOH-Zn degrdn. of 100 g. I as described previously, the resulting NaHCO₃-sol. fraction distd. at 220-4°/0.05 mm., and the yellow viscous distillate (1.8 g.) recrystd. 9 times from cyclohexane gave 1 g. (2%) isodecarboxyterracinoic acid (7-hydroxy-3-methylindanone-2-acetic acid) (X), colorless plates, m. 111.5-12.5°; pKa 5.5 and 9.7; λ_{\max} . 225 (4.04), 319 (3.56) in EtOH-HCl, 237 (4.34), 262 (3.94), 363 m μ (log ϵ 3.96) in EtOH-NaOH; λ_{\max} . 5.88, 5.99 μ (CHCl₃); gave a purple color with alc. FeCl₃. X (150 mg.) treated 2 h. at 0-20° with 75 mg. CH₂N₂ in 20 cc. Et₂O yielded 100 mg. Me ester, n_D25 1.5470, gave a purple FeCl₃ test. X reacts readily with 2 g.-atoms Br in glacial AcOH to yield HBr and an oily product, presumably the 2-Br deriv. of X which gave refluxed in N alkali a cryst. Br-free solid, insol. in aq. NaHCO₃ and giving a violet FeCl₃ test. X (140 mg.) fused 8 min. with 2 g. NaOH and 2 g. KOH at 325° yielded 30 mg. solid acid (not further investigated) and 10 mg. m-EtC₆H₄OH. Freshly sublimed 1,8-C10H₆(OH)₂ (18 g.) in 75 cc. abs. EtOH hydrogenated at 60° and 50 lbs. pressure over 6 g. Raney Ni yielded 10.9 g. 8-hydroxy deriv. of 1-tetralone (XI), colorless oil, b_{0.07} 82°, n_D20 1.5871, λ_{\max} . 260 (3.97), 335 m μ (log ϵ 3.49). Freshly sliced Na (4.2 g.) and 13 g. XI in 35 cc. EtOAc refluxed 4 h. with stirring under dry N, the mixt. cooled, acidified with 5% AcOH and crushed ice, and extd. with seven 100-cc. portions Et₂O, the ext. washed with satd. aq. NaHCO₃, dried with MgSO₄, and evapd., and the oily residue treated with a satd. soln. of Cu(OAc)₂ in MeOH yielded 7.8 g. Cu salt (XII) of the 2-Ac deriv. (XIII) of XI, m. 254-5° (decompn.) (from C₆H₆). A portion of the XII decompd. with 10% H₂SO₄, the mixt. extd. with Et₂O, the ext. washed with NaHCO₃, dried, and evapd., and the residue distd. evaporatively at 150°/0.05 mm. gave XIII, λ_{\max} . 267 (3.74), 348 m μ (log ϵ 4.09), λ_{\max} . 5.87, 6.25-6.35 μ . I.HCl (15 g.) treated with 15.2 g. dry HCl in 600 cc. dry Me₂CO cooled to -5°, the mixt. let stand 11 h. to reach a const. rotation of $[\alpha]_{D20}$ -300° and dild. with 700 cc. Et₂O, and the yellow ppt. (12.9 g.) recrystd. from 250 cc. BuOH-dioxane (1:2) yielded 9.4 g. (50%) pure acetonylanhydroterramycin (XIV) hydrochloride, decompd. at 225° without melting, $[\alpha]_{D20}$ -455° (MeOH), pKa 3.8, 5.5, and 7.2; the absence of the Me₂CO carbonyl band in the IR spectrum, together with the rapid elimination of Me₂CO in acid or basic soln. led to the conclusion that the Me₂CO is bonded to the amide N in XIV; in alk. EtOH, the UV spectrum undergoes a rapid reversible change to a stable curve which is identical with that of a mixt. of apoterramycins. The distn. of an aq. soln. of XIV gave

Me₂CO, identified as the 2,4-dinitrophenylhydrazone, m. 126-7°. XIV (4 g.) in 20 cc. H₂O adjusted rapidly with 5% aq. NaHCO₃ to pH 5, and the amorphous ppt. recrystd. from Me₂CO gave anhydroterramycin as an acetone solvate, m. 180-90° (decompn.) (dried at 100°/0.1 mm.), [α]_D²⁵ 52° (from 1:1 MeOH-dioxane); it gave a green color with FeCl₃, a red-green color with HNO₂, and an intensive blue color with dil. Br solns.; λ_{max}. 271 (4.56), 425 mμ (log ε 3.80) in acid EtOH, λ_{max}. Nujol 5.83 μ. 1,8-Dihydroxyanthraquinone (3 g.), m. 193-4°, in 50 cc. 4% aq. NaOH hydrogenated 2.5 h. over 1 g. 5% Pd-C, the mixt. filtered rapidly into excess dil. HCl, and the cryst. ppt. recrystd. with C from aq. Me₂CO yielded 1.2 g. 8,9,10-trihydroxy-1-oxo-1,2,3,4-tetrahydroanthracene, m. 180-2°, and 0.5 g. 2nd crop, m. 164-7°; anal. sample, red needles, m. 186-8°; pK_a 8.3; λ_{max}. 267 (4.55), 425 mμ (3.83) in acid MeOH, λ_{max}. 3.0, 6.15 μ. IV in anhyd. Me₂CO-HCl let stand overnight at 5°, the soln. dild. with Et₂O, and the cryst. ppt. recrystd. twice from HCONMe₂-EtOH and dried at 100°/0.1 mm. over P₂O₅ gave benzenesulfonylanhydroterramycinonitrile (10-benzenesulfonyl-4-dimethylamino-1,4,4a,5,12,12a-hexahydro-3,5,11,12a-tetrahydroxy-6-methyl-1,12-dioxo-2-naphthacenitrile), yellow prisms, [α]_D²⁵ -390° (HCONMe₂); pK_a 6.3; λ_{max}. 275 (4.58), 400 mμ (log ε 3.88). I.HCl (50 g.) in 100 cc. 0.5N HCl heated 9 h. at 60°, the clear yellow soln. dild. to 375 cc. and adjusted with 10% aq. NaOH to pH 3.5, the amorphous filtrate of α- (XV) and β-apoterramycin(3-[(4-carbamoyl-2-dimethylamino-3,6-dihydroxy-5-oxo-3-cyclohexen-1-yl)hydroxymethyl]-1,8-dihydroxy-4-methyl-2-naphthoic acid γ-lactone) (XVI) filtered off, washed with H₂O, and dissolved in 500 cc. hot EtOH, the soln. let stand 24 h., the solid deposit filtered off, suspended in 50 cc. H₂O, and dissolved by the addn. of 12N HCl to pH 1, the soln. filtered and concd. in vacuo, the residual sirup let stand 24 h., the cryst. HCl salt filtered off, washed with ice-cold 6N HCl, and dissolved in H₂O, the soln. adjusted to pH 3.5, and the ppt. recrystd. from EtOH gave 16 g. pure XV, m. 190-200° (decompn.) (dried 3 h. at 100°/0.1 mm.), [α]_D²⁵ -45° (HCONMe₂); λ_{max}. 250 (4.77), 377 mμ (log ε 3.87) in acid EtOH, λ_{max}. dioxane 5.82 μ; HCl salt, m. 180-95° (decompn.) (dried at 80°/10 mm. in dry HCl), [α]_D²⁵ 123° (EtOH); pK_a 4.0, 5.1, and 8.4; λ_{max}. Nujol 5.75-5.85 μ. The filtrate from the first recrystn. of the XV-XVI mixt. concd. in vacuo to 100 cc., acidified with 60 cc. 2.5N HCl, and cooled 24 h. to 5° yielded 21 g. XVI HCl salt in 2 crops; the crude salt recrystd. twice by dissolving in hot EtOH and adding 0.4 vols. H₂O, and the ppt. dried in a slow stream dry HCl at 50°/5-10 mm. gave pure XVI.HCl, m. 195-205° (decompn.), [α]_D²⁵ -28° (EtOH); pK_a 3.6, 5.2, and 7.8;

λ_{max} . 248 (4.78), 375 $\text{m}\mu$ ($\log \epsilon$ 4.00);
 λ_{max} . Nujol 5.70, 6.0 μ (shoulder). XVI was not obtained in cryst. form. XV and XVI are readily interconvertible at pH 1 and 8. XVI.HCl formed an extremely stable solvate with MeOH which is not removed on prolonged drying at 100° in vacuo. XVI.HCl (1.0 g.) in 2.5 cc. pyridine and 2.5 cc. Ac₂O heated 1.5 h. at 100°, the mixt. poured on ice, the amorphous ppt. filtered off, washed with H₂O, dried in vacuo over CaCl₂, and dissolved in 150 cc. dry Et₂O, and the soln. treated with dry HCl gave 0.5 g. ppt. which yielded recrystd. twice from 5 cc. MeOH 0.10 g. pure tri-Ac deriv. of XVI.HCl crystg. with 0.5 mol H₂O, m. 201.5-2.5° (decompn.) (dried 2 h. at 80°/0.1 mm.); pKa 3.4 and 7.2. The presence of small quantities of XV and XVI in the presence of large amts. of I or terrinolide is readily demonstrated by paper chromatog. in a descending system with 5:4:1 H₂O-BuOH-AcOH showing the following R_f values: I 0.42, XV 0.21, XVI 0.74, and terrinolide 0.91; all 4 compds. show fluorescence under UV light. In this manner, as little as 1% XVI could be detected in XV. XV (4 g.), 20 g. NaOH, and 30 g. KOH powd. in a mortar fused 10 min. at 240°, the melt cooled, dissolved in 400 cc. ice and H₂O, acidified with 6N H₂SO₄ to pH 2, and extd. with five 150-cc. portions Et₂O, the ext. dried with CaCl₂ and concd. to about 5 cc. on a steam bath, the cryst. deposit filtered off, washed with a few cc. cold dioxane, and combined with a 2nd crop crystals which pptd. from the mother liquor, and the total product (0.42 g.) sublimed at 125°/0.02 mm. yielded 50 mg. red crystals which were resublimed, recrystd. twice from hot dioxane, and sublimed again to give 22 mg. pure 2,5-dihydroxybenzoquinone, λ_{max} . 285 $\text{m}\mu$ ($\log \epsilon$ 4.27) in acid-EtOH, λ_{max} . 6.05, 61.4 μ ; di-Ac deriv., m. 159-60°; the residue from the sublimation of the crude fusion product recrystd. 3 times from dioxane gave 20 mg. relatively insol. yellow product, apparently a mixt. of 4,5-dihydroxy-1-methyl-2,3-naphthalenedicarboxylic acid and its anhydride, m. 260-70° (with prior decompn.), λ_{max} . 5.47, 5.57, 5.80, 6.12 μ ; gave heated with aq. dioxane substantial amts. VI; the mother liquors from the acid-anhydride mixt. recrystd. from dioxane and then from aq. MeOH yielded 100 mg. pure VI, m. 235° (decompn.). IV (5 g.) in 50 cc. MeOH satd. at 0° with dry HCl, the mixt. heated 1 h. at 60°, and the colorless cryst. ppt. which appeared to be a half-HCl salt dried (3.2 g.) and recrystd. from HCONMe₂EtOH-H₂O yielded benzenesulfonylapoterramycinonitrile [3-(4-cyano-2-dimethylamino-3,6-dihydroxy-5-oxo-3-cyclohexene 1-yl)hydroxymethyl-8-benzenesulfonyl-1-hydroxy-4-methyl-2-naphthoic acid γ -lactone] monohydrate, rectangular plates, [α]_D₂₅ 29° (HCONMe₂), pKa 5.7 and 8.5; λ_{max} . Nujol 5.75 μ . I.HCl (50 g.) in 100 cc. 0.5N HCl heated at 60° and aerated 9 days at the rate of 2 cc./min., the solid deposit filtered off, the filtrate aerated again 5 days,

and the addnl. 7.5 g. solid product combined with the 1st crop recrystd. from aq. iso-PrOH yielded 25 g. crude terrinolide [1,8-dihydroxy-4-methyl-3-(4-carbamoyl- α ,2,3,5-tetrahydroxybenzyl)-2-naphthoic acid γ -lactone] (XVII) in 3 crops; an anal. sample was obtained by recrystn. 3 times from MeOH-free Me₂CO and drying 5 h. at 100°/0.1 mm., m. 210-15° (decompn.), $[\alpha]_{D25}$ -16° (1:1 MeOH-0.1N HCl); λ_{max} . 249 (4.75), 360 m μ (log ϵ 4.08), λ_{max} .Nujol 5.85, 6.05 μ ; pKa 4.6 and 7.5; sol. in EtOH, Me₂CO, and aq. NaHCO₃, insol. in C₆H₆, Et₂O, and H₂O; gave a green FeCl₃ test, a pos. Wildi catechol test, and a pos. Fehling test; increased the acidity of H₃BO₃ similarly as 1,8-C₁₀H₆(OH)₂; formed solvates with H₂O and MeOH which were stable at 100°/0.1 mm. for many hrs. XVII was also obtained in comparable yield but slower by heating an acid soln. of I 1-2 mo at 60° in a loosely stoppered flask; small amts. of O are desirable; no XVII was formed under N, while with excess air or O, a tarry intractable polymeric product was formed. XVII (1 g.), 0.5 g. dry NaOAc, and 5 cc. Ac₂O heated 1 h. on the steam bath, the mixt. cooled, the tan colored cryst. deposit **stirred** into 80 cc. ice-water, and the product filtered off and recrystd. twice from Me₂CO-MeOH gave the penta-Ac deriv. (XVIII) of XVII, colorless needles, m. 229-30°, $[\alpha]_{D25}$ 34° (Me₂CO), sol. in CHCl₃ and Me₂CO, slightly sol. in EtOH, gave a neg. FeCl₃ test and was only slowly sol. in dil. NH₄OH. XVII (3 g.) and 40 cc. MeI in 600 cc. Me₂CO refluxed 4 days with 30 g. K₂CO₃, the hot soln. filtered, dild. with 20 cc. H₂O, and concd. in vacuo, and the residual viscous oil washed with H₂O, and recrystd. from Me₂CO and then from Me₂CO-EtOH gave 1.6 g. pure penta-Me deriv. (XIX) of XVII, m. 225-7°, $[\alpha]_{D25}$ -9.2° (Me₂CO), insol. in alkali; λ_{max} . 250 (4.71), 362 m μ (log ϵ 3.94).

XIX (0.3 g.) refluxed 4 h. with 5 cc. 15% HCl and 25 cc. glacial AcOH, and the solvent removed in vacuo left a mixt. of tri-Me derivs. of XVII; a 0.2 g. portion suspended in 5 cc. 2% aq. NaHCO₃ and dissolved with the min. amt. 10% aq. NaOH, the soln. cooled to 0° and treated portionwise with 7.2 cc. 5% aq. KMnO₄, the MnO₂ dissolved with NaHSO₃, the soln. acidified and extd. with Et₂O, the ext. concd. to dryness, and the oily residue recrystd. from EtOH and then sublimed at 175°/0.05 mm. yielded 6 mg. 1,8-dimethoxy-4-methylnaphthalene-2,3-dicarboxylic acid, colorless crystals, m. 230-5°, sublimed at 165°; sol. in hot aq. NaOH; λ_{max} . 247 (4.42), 308 (3.79), 338 m μ (3.74), λ_{max} .CHCl₃ 5.50, 5.67 μ ; an aq. soln. acidified did not give the acid, but pptd. the anhydride on heating; gave a neg. FeCl₃ test. I hydrochloride (10 g.) in 300 cc. 0.1N HCl refluxed 10 days under N, the partially cryst. brown ppt. recrystd. 4 times from hot HCONMe₂, and the resulting colorless crystals (2.5 g.) contg. solvent of crystn. **stirred** 3 days with Et₂O and dried at

100°/0.1 mm. gave racemic XVII, white, insol. in the common org. solvents, the UV spectrum was identical with that of (-)-XVII. Racemic XVII in pyridine treated with Ac₂O gave the racemic XVIII in a low-melting form, m. 198-200° (decompn.) (from EtOH), which was converted on prolonged heating in EtOH to a relatively insol. stable form, m. 222-3° (decompn.); the 2 forms showed identical IR spectra in dioxane, but the spectra differed slightly in mull. Racemic XVII methylated 48 h. as described for (-)-XVII yielded the racemic XIX, m. 234.5-5.5°, as well as a tetra-Me ether, m. 238-9°; the 2 ethers were readily sepd. by chromatog. on Florisil with Me₂CO; the IR spectra of the 2 XIX in dioxane are identical. XVII (10 g.) refluxed 72 h. under N with 120 cc. 12N H₂SO₄, the insol. material filtered off, washed free of sulfate with H₂O, dried in vacuo (7 g.), dissolved in 150 cc. Me₂CO, filtered, and chromatographed on 150 g. acid-washed Florisil, the eluate collected until pale yellow in color and acidified with 100 cc. 2N HCl, the Me₂CO removed in vacuo at room temp., and the cryst. residue (3.75 g.) recrystd. from EtOH and then from EtOH-C₆H₆, and dried at 100°/0.1 mm. yielded 2.5 g. pure racemic decarboxamidoterrinolide [1,8-dihydroxy-4-methyl-3-(α ,2,3,5-tetrahydroxybenzyl)-2-naphthoic acid γ -lactone] (XX), decompd. at 215-50° without melting; pK_a 4.7, and 10.2; λ_{max} . 247 (4.70), 375 m μ (log ϵ 4.00), λ_{max} . dioxane 5.75 μ ; gave a pos. Wildi test, a pos. aminoantipyrine test, a green color with alc. FeCl₃, a deep red color on aeration in NH₄OH (reversed by NaHSO₃); was susceptible to oxidn. in alkali; sol. in EtOH and Me₂CO, insol. in C₆H₆ and CHCl₃; formed a very stable solvate with MeOH; gave on alkali fusion VI. XVI (2 g.) in 100 cc. 12N HCl refluxed 24 h. in a slow stream of O-free N and the amorphous ppt. filtered off (1.1 g.) and recrystd. from Me₂CO yielded 1.0 g. (70%) XX. The penta-Me deriv. (XXI) of XX, m. 150-1° (from EtOH), was prepd. as described for XIX, insol. in cold. alc. NaOH, sol. in 10% aq. alc. NaOH on prolonged heating at 120°; acidification of the cooled soln. pptd. the lactone directly. The penta-Ac deriv. of XX, m. 243-5° (decompn.) (from Me₂CO-petr. ether), was prepd. as described for XVIII. XX (1 g.) in 15 cc. anhyd. pyridine and 5 g. p-MeC₆H₄SO₂Cl kept 28 h. at 25° the mixt. poured into 125 cc. H₂O, and the amorphous ppt. dried, dissolved in 25 cc. Me₂CO, and dild. with 25 cc. EtOH (a 2nd crop was obtained on concn.) gave 2.6 g. pure penta-p-toluenesulfonyl deriv. of XX, m. 154-8° (from Me₂CO-C₆H₆ and dried 24 h. at 100°/0.1 mm.). KMnO₄ (29 g.) added portionwise during 2 h. with stirring to 3.5 g. XXI in 40 cc. pyridine and 15 cc. H₂O at 75°, the mixt. treated with 20 cc. pyridine and 25 cc. H₂O, and **stirred** 1 h., the excess KMnO₄ destroyed with H₂O₂, the mixt. concd. in vacuo with repeated addn. of H₂O, the aq. suspension filtered and adjusted to pH 2, and the yellow amorphous product recrystd. twice from aq. EtOH gave 0.23

g. decarboxamidoterrinolidic acid pentamethyl ether [1,8-dimethoxy-3-(α -hydroxy-2,3,5-trimethoxybenzyl)naphthalene-2,4-dicarboxylic acid γ -lactone] (XXIIa) or possibly XXII, pale yellow crystals, m. 210-12.5° (dried at 100°/0.1 mm.); λ_{max} . 256 (4.56), 340 m μ (log ϵ 3.92), λ_{max} .CHCl₃ 5.75-5.8 μ . XXI (1 g.) dissolved in 20 cc. concd. HNO₃ at its f.p., the soln. kept 7 days at 30° and then 6 days at 25°, the amorphous ppt. (0.20 g.) filtered off and sublimed at 75°/0.1 mm. to yield 0.10 g. (CO₂H)₂ and the unsublimed residue recrystd. 4 times from Me₂COC₆H₆ and sublimed at 140°/0.05 mm. yielded 50 mg. pure 3-methoxy-6-methylpyromellitic dianhydride, m. 270-1°; showed in the IR spectrum 4 CO bands of progressively increasing intensity between 5.35 and 5.60 μ , while the Na salt showed only carboxylate ion absorption at 6.30; λ_{max} . 252 (4.19), 400 m μ (log ϵ 3.90) in concd. H₂SO₄. XXI (0.42 g.) in 20 cc. THF treated with 20 cc. 0.5M LiAlH₄ in Et₂O, the mixt. dild. with 150 cc. Et₂O, the turbid soln. **stirred** 3 h. at 25° the excess LiAlH₄ decompd. carefully with 50 cc. H₂O, the aq. layer extd. with three 100-cc. portions Et₂O, the combined Et₂O solns. dried with CaCl₂ and evapd. to dryness, and the residue recrystd. 3 times from Et₂O yielded 0.10 g. pure 2-hydroxymethyl-4-methyl-3-(α -hydroxy-2,3,5-trimethoxybenzyl)-1,8-dimethoxynaphthalene (XXIII), m. 114-15°, λ_{max} . 238 (4.85), 292 m μ (log ϵ 3.94). XXIII (50 mg.) in 1 cc. dioxane contg. 0.05 cc. 6N HCl heated 1.5 h. at 100°, the red soln. evapd. to dryness in vacuo, and the amorphous residue sublimed at 220°/0.1 mm. and recrystd. twice from EtOH yielded 8 mg. 1,3-dihydro-7,8-dimethoxy-4-methyl-3-(2,3,5-trimethoxyphenyl)-naphtho[2,3-c]furan, m. 148.8-50.8°; λ_{max} . 237 (4.87), 292 (3.94), 370 m μ (2.39). Zn dust (50 g.) added portion-wise to 50 g. I.2H₂O in 300 cc. glacial AcOH with stirring, the mixt. **stirred** 8 h. at 30° and filtered, the filtrate freeze-dried, the amorphous yellow product dissolved in 300 cc. MeOH contg. 25 cc. concd. HCl, the soln. poured into 500 cc. H₂O, the resulting slurry (pH 1) extd. with four 200-cc. portions Et₂O, the ext. evapd. to dryness at 10°, and the solid residue sepd. from a little H₂O and triturated with Me₂CO yielded 11.4 g. (27%) de(dimethylamino)terramycin-[1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,10,12,12a-hexahydroxy-6-methyl-1,11-dioxo-2-naphthacenecarboxamide] (XXIV), pale yellow plates, m. 216-17° (decompn.) (from Et₂O and then MeOH-CHCl₃), [α]_D²⁵ -137° (MeOH), -47° (Me₂CO); pK_a 6.8 and 8.9; λ_{max} . 261 (4.25), 363 m μ (log ϵ 4.17). XXIV (0.5 g.) in 10 cc. MeOH and 1 cc. concd. HCl boiled 1 min., the soln. cooled, and the heavy yellow cryst., ppt. filtered off and recrystd. from dioxane-MeOH gave 0.4 g. pure anhydrode(dimethylamino)terramycin (XXV), m. 232-3°

(decompn.), $[\alpha]_{D25} 170^\circ$ (dioxane); the UV spectrum is substantially identical with that of anhyd. XIV in acid or alk. EtOH soln. XXV (0.23 g.) dissolved in 2 cc. 0.5N NaOH under N, and the soln. acidified gave de(dimethylamino)apoterramycin, colorless crystals, recrystd. from HCONMe₂MeOH; pKa 4.6 and 8.1; λ_{max} . 251 (4.63), 375 (4.06) in acid EtOH; λ_{max} . Nujol 5.75, 6.05 μ . I, Zn, and AcOH in the proportions used for the prepn. of XXIV **stirred** 4 days at 25-30°, the mixt. filtered, the filtrate concd., the residual viscous sirup **stirred** with 500 cc. H₂O, the amorphous ppt. filtered off, washed with H₂O, dried, and extd. exhaustively in a Soxhlet app. with Et₂O, the ext. evapd. to dryness, and the amorphous residue triturated with Me₂CO and then recrystd. from Me₂CO yielded 21 g. (50%) de(dimethylamino)deoxyterracycin (1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,10,12-pentahydroxy-6-methyl-1,11-dioxo-2-naphthacenecarboxamide) (XXVI), contg. 0.5 mol Me₂CO of crystn., m. 180-1° (decompn.) when placed in a bath at 165° and heated at 2°/min.; prolonged drying at 80° removed only a portion of the Me₂CO of crystn.; pKa 7.1 and about 11.5; λ_{max} . 263 (4.31), 320 m μ (log ϵ 4.22); λ_{max} . 5.80, 6.08; attempted recrystns. from MeOH, CHCl₃, AcOH, or dioxane yielded only an amorphous product unless Me₂CO was present. XXVI (2 g.) dissolved in 50 cc. 0.5N alc. KOH, the resulting semisolid gel treated after 12 h. dropwise with glacial AcOH, and the resulting granular cryst. ppt. recrystd. twice from AcOH-H₂O, and twice from aq. EtOH, and dried 18 h. at 100°/0.1 mm. gave isodeoxyde(dimethylamino)-terracycin [4,4a,5,6,7,8-hexahydro-1,3,5-trihydroxy-6-(7-hydroxy-3-methylphthalidyl)-8-oxo-2-naphthamide (XXVII), decompd. without melting at 210-20°; pKa 7.2 and 9.2; λ_{max} . 242 (4.16), 256 (4.14), 314 m μ (log ϵ 4.29); λ_{max} . 5.75, 6.15 μ . XXVII (100 mg.) heated 5 min. at 0.1-0.5 mm. pressure in a Pyrex tube in a metal bath at 400°, and the volatile material collecting in the cool section of the tube distd. at 100°/0.1 mm. yielded 3.5 mg. 7-hydroxy-3-methylphthalide, m. 108-10° (from H₂O). I.2H₂O (10 g.) added in portions with stirring to 80 cc. H₂SO₄ in 30 cc. H₂O at 10°, the soln. warmed to room temp., **stirred** overnight under N, and slowly dild. with gentle intermittent stirring with 800 g. clean ice, the resulting mixt. of cryst. and red amorphous products filtered off, washed with H₂O and then with Me₂CO, dried in vacuo (1.8 g.), suspended in 20 cc. HCONMe₂ and filtered, and the filter residue washed with small vols. HCONMe₂ and then with 100 cc. Me₂CO gave 280 mg. (3%) terrarubein, C₂₂H₂₀N₂O₆ (XXVIII), red-orange needles, decompd. without melting at 250-60°, λ_{max} . 255 (4.47), 435 m μ (log ϵ 3.94) in AcOH-dioxane-EtOH; λ_{max} . 5.80, 6.07, 2.9-3.1; sol. in hot HCONMe₂ with some decompn.; slightly sol. in glacial AcOH, and virtually insol. in the

other common solvents. XXVI (2.1 g.) in 65 cc. MeOH satd. with HCl let stand 3 h., and the resulting mixt. (1.83 g., 97%) of microcryst. and amorphous product recrystd. twice from HCONMe₂ yielded 50% de(dimethylamino)terrarrubein (XXIX), charred and decompd. at 200-300° without melting; slightly sol. in hot glacial AcOH, quite sol. in boiling PhNO₂ with decompn., virtually insol. in the other common org. solvents except HCONMe₂; λ_{max} . 271 (4.41), 315, 355, 450 m μ (log ϵ 4.00-4.05) in 1:9 AcOH-EtOH; λ_{max} . Nujol 5.93, 6.02 μ ; was also obtained by the treatment of XXVI with hot glacial AcOH or hot HCO₂H. Purified Zn dust (20 g.) mixed with 200 mg. cryst. XXIX, the mixt. heated to nearly red heat in a slow stream H, the distd. products (6.0 mg.) combined, recrystd. from CHCl₃ and xylene, and sublimed in vacuo at 180-200° yielded pure naphthacene, sublimed without melting at 290°. XXVIII (40 mg.) treated similarly with 3.5 g. purified Zn dust and the crude distillate sublimed twice gave 0.25 mg. pure naphthacene. I treated with strong cold mineral acids yielded small amts. of XVIII which must be a dimethylaminosubstituted XXIX. Zn dust distn. of I gave only a trace of an uninformative hydrocarbon mixt.

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48:60340 Original Reference No. 48:10675e-i,10676a-i,10677a

Stereochemistry of the β -phenylserines: improved preparation of allophenylserine. Shaw, Kenneth N. F.; Fox, Sidney W. (Iowa State Coll., Ames). Journal of the American Chemical Society, 75, 3421-4 (Unavailable) 1953. CODEN: JACSAT. ISSN: 0002-7863.

AB cf. preceding abstr. The prepn. of phenylserine (I) and allo-I (II) by condensation of BzH and H₂NCH₂CO₂H (III) has been studied by the use of paper chromatography. The isomers were prepd. in comparable quantities with a 1-hr. condensation period; the proportion of II decreased sharply with longer reaction time. II forms a hemihydrate, and a poorly sol. addn. compd. with dioxane which was used to sep. II from I. The HCl salts, the Me, Et, Pr, and iso-Pr ester HCl salts, and the corresponding esters of I and II were prepd. Threonine (IV) and allothreonine (V) were sepd. by paper chromatography under the same conditions as I and II. Aq. solns. of I and II were applied to No. 4 Whatman paper, the resulting spots let dry at room temp., the paper stapled to a cylinder, the upright cylinder placed in 125-50 cc. of the upper H₂O-poor layer from a mixt. of 200 cc. BuOH, 150 cc. H₂O, 25 cc. Me₂CO, and 25 cc. concd. NH₄OH, the liquid allowed to ascend 3-6 hrs. at room temp., the solvent front penciled, the cylinder dried in air at room temp., and the opened sheet sprayed uniformly with 0.2% ninhydrin soln. in BuOH satd. with H₂O and dried 10-15 min. at 80° to give orange-brown spots which darkened to violet within 24 hrs. A similar paper chromatogram of spots of 0.1% aq. solns. of IV and V

(5.5 hrs. ascent) gave with ninhydrin blue-violet spots showing Rf values of 0.18-0.19 and 0.13-0.14, resp. III (30.0 g.) and 24.0 g. NaOH in 100 cc. H₂O treated with cooling to 15° and rapid stirring with 84.9 g. BzH in 1 portion, the condensation cake let stand different periods of time with various batches, treated dropwise at 15° during 0.5 hr. with 50.0 cc. concd. HCl, the mixt. **stirred** 1 hr., filtered, the filter cake thoroughly mixed with three 200-50-cc. portions of boiling 95% EtOH, the resulting slurry filtered each time, and the washed product dried to const. wt. over Anhydrone at 50-60° and 10-15 mm. gave a mixt. of I and II the proportions of which were detd. by paper chromatography. In two 1-hr. runs acidification of the mixt. gave a thin slurry; further agitation caused thickening to a smooth paste and then to large lumps; the clear pale yellow supernatant, contg. only a few cc. BzH, was cooled 2 hrs. to 5°, filtered off, and the solid filter residue sucked dry and worked up further as described to give 33.4 g. (46%) mixt. contg. 55-60% I and 40-5% II; from the aq. filtrate and EtOH washings was recovered 15-25% III. Three batches acidified after 4 hrs. thickened to a stiff paste which was refrigerated 1-24 hrs. at 5°, suctiondried, the filter cake **stirred** with 100 cc. boiling EtOH, the resulting solid cake slurried with 150 cc. boiling EtOH, filtered, and the product treated in the usual manner to give 44.3 g. (61%) mixt. contg. 80-5% I and 15-20% II; 5-10% III was recovered. With a condensation time of 24 hrs., 52.7 g. (73%) I was the only reaction product, with a recovery of 2-4% III. In a similar 60-hr. run the yield of the exclusively formed I was 49.0 g. (68%), with 1-2% III recovered. I (2.500 g.) dissolved in 30 cc. boiling H₂O, and the soln. dild. with 30 cc. boiling EtOH gave 2.175 g. I.H₂O, layered **hexagonal** plates (dried 18 hrs. over Anhydrone at 50-60° and about 20 mm. pressure). II (2.500 g.) in 35 cc. boiling H₂O dild. with 35 cc. boiling dioxane, the mixt. refrigerated overnight at 5°, filtered, and the filter residue washed with cold 50% aq. dioxane and dried in air at room temp. gave 2.998 g. (97%) II-dioxane adduct (VI) after drying, unchanged by heating 2 hrs. at 77° and about 0.1 mm. over **P205**. VI (11.124 g.) in 100 cc. boiling H₂O gently simmered 5-10 min., the vessel scratched with cooling, and the resulting 5.972 g. (63%) II.0.5H₂O, **hexagonal** microprisms, recrystd. from hot H₂O, washed with ice H₂O, and dried in air at room temp. gave the pure hemihydrate; slow evapn. of aq. II at room temp. gave also the hemihydrate; the filtrate from the crude II.0.5H₂O heated to boiling and dild. with an equal vol. of boiling dioxane gave 2.856 g. (26% recovery) VI. II (2.500 g.) in 50 cc. hot H₂O dild. with 50 cc. boiling Me₂CO, the soln. refrigerated overnight at 5°, filtered, and the residue washed with 50% aq. Me₂CO, Me₂CO, and Et₂O, and dried 12 hrs. at 50-60° and 10-15 mm. over Anhydrone yielded 1.818 g. (73% recovery) anhyd. II, long

fibrous needles; recrystn. from hot H₂O alone yielded anhyd. II also, if the soln. was let cool slowly at room temp. with frequent swirling. The crude product from a 1-hr. condensation of BzH and III contg. 55-60% I and 40-5% II (89.2 g.), recrystd. from 890 cc. boiling H₂O, gave 26.7 g. (30% recovery) I contg. less than 5% II; the aq. filtrate heated to boiling and dild. with an equal vol. of dioxane pptd. 43.0 g. (39% recovery) II contg. about 5% I; the 50% dioxane filtrate concd. in vacuo to 170 cc., heated to boiling, and treated with an equal vol. of boiling EtOH gave 18.9% (21% recovery) I contg. only traces of II; the 50% EtOH filtrate contained about 6.5 g. (7%) mixed I and II; the 2 I fractions, combined and recrystd. twice from 50% EtOH in the usual manner, gave pure I; the VI middle fraction recrystd. from 50% dioxane and then from 50% EtOH, gave pure II; all the filtrates combined, concd. in vacuo, and treated with EtOH gave 15.2 g. (17% recovery) mixt. of 9.1 g. I and 6.1 g. II, and a 2nd crop of 5.4 g. (7% recovery) mixt. of 3.2 g. I and 2.2 g. II; the residual filtrate contained 2.4 g. (2% recovery) mixt. of 1.2 g. I and 1.2 g. II. Anhyd. I or II (1.0182 g.) suspended in 18 cc. anhyd. dioxane, treated 15 min. with a brisk stream of dry HCl, and the clear solns. dild. with equal vols. of dioxane and then with Et₂O to incipient turbidity, and refrigerated yielded 1.918 g. (88%) I.HCl and 2.030 g. (93%) II.HCl, resp.; the HCl salts were poorly sol. in fresh boiling dioxane and were recrystd. from MeOH-Et₂O to give pure samples of I.HCl, m. 160°, and of II.HCl, m. 159°. Into a suspension of 3.624 g. anhyd. I or II in 36 cc. appropriate refluxing alc. was passed a vigorous stream of dry HCl for 2.5-3 hrs., the clear soln. evapd. almost to dryness, the residual oil or paste taken up in a small vol. of the parent hot alc., and the soln. dild. with EtOH to incipient crystn. to yield the corresponding esters; the ester HCl salt which pptd. during the HCl treatment was redissolved in the hot parent alc., the soln. refrigerated overnight, filtered, and the residues washed with Et₂O and dried at 50°; small 2nd crops were obtained from the filtrates. In this manner were prepd. the following alkyl ester HCl salts of I (alkyl group, total wt. in g. of crude product, % yield, and m.p. given): Me, 4.360, 94, 160° (decompn.); Et, 4.796, 98, 140°; Pr, 4.679, 90, 131°; iso-Pr, 4.947, 95, 164°; and the following alkyl ester-HCl salts of II: Me, 4.485, 97, 180° (decompn.); Et, 4.783, 96, 178° (decompn.); Pr, 5.031, 97, 160°; and iso-Pr, 5.069, 98, 159° (decompn.). Each ester-HCl salt in Et₂O treated with NH₃ gave the corresponding free ester. In this manner were obtained the following alkyl esters (alkyl group, crystal form, % yield, and m.p. given) of I: Me, needles, 75, 62°; Et, mica plates, 77, 84°; Pr, needles, blades, 85, 59°; iso-Pr, needles, blades, 89, 75°; and of II: Me, mica plates, 89, 110°; Et, needles, 92, 86°; Pr, needles, 89, 63°; and iso-Pr, needles, 85, 75°.

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48:7161 Original Reference No. 48:1318a-i,1319a-i,1320a-i The nature of light-induced degradation products of diazo derivatives. IV. The light reaction of o-quinonediazides: photosyntheses of cyclopentadiene derivatives. Sus, Oskar; Hoffmann, Hinrich; Rosenberger, Siegfried; Kostka, Rudolf (Kalle & Co., Wiesbaden-Biebrich, Germany). Ann., 579, 133-58 (Unavailable) 1953. OTHER SOURCES: CASREACT 48:7161.

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 42, 4154i. 6-Nitro-1,2-naphthoquinone-2-diazide (2-diazo-6-nitro-1(2H)-naphthalenone) (I) in 4.5 l. AcOH and 240 cc. H₂O was filtered through C and the filtrate, in sealed fermentation vessels, exposed to sunlight or ultraviolet light at 0°. The reaction was complete when an aliquot no longer coupled with phloroglucinol to form an azo dye. The soln., concd. in vacuo, gave about 8.5 g. (crude) 5-nitro-1-indenecarboxylic acid (II), pale yellow cryst. threads, m. 188-9° (from AcOH), which when heated to 185-210° gave CO₂ and 5-nitroindene (III), m. 74-5° (by sublimation), also prepd. by heating II in HCO₂NMe₂ at 45-90°. Hydrogenation of III in EtOH by shaking with Raney Ni, steam-distg., and cooling to 0° gave 5-aminohydrindene, m. 36°; Ac deriv., m. 106° (from C₆H₆-gasoline). 1-Amino-2-hydroxy-7-methoxynaphthalene (10 g.) in 10% alc. HCl with 10 cc. iso-AmONO gave 9.35 g. of an HCl salt, which, when **stirred** with H₂O or on attempted recrystn. from much H₂O gave 7-methoxy-1,2-naphthoquinone-1-diazide, C₁₁H₈O₂N₂, yellow needles, m. 103-4° (from 50% alc.), which when irradiated 8 hrs. gave 5-methoxy-3-indenecarboxylic acid (IV), m. 160-1° (purified by soln. in aq. NaHCO₃, pptn. with HCl, and crystn. from C₆H₆ or aq. MeOH); the corresponding 5-methoxyindene (V), bll 155-60°, with nerolinlike odor, was formed by heating IV in HCONMe₂ under N. When the decarboxylation of IV by direct heating at about 185°, was attempted, C₂₂H₂₀O₆, a dimer of IV, m. 235-6°, was formed. IV (0.3 g.) in AcOEt with CH₂N₂ in Et₂O, followed by shaking successively with 2% AcOH, H₂O, 5% NaHCO₃ and H₂O, drying the Et₂O soln. with Na₂SO₄, and evapg. gave Me 1,3a,4,9a-tetrahydroindeno[1,2-c]pyrazole-4-carboxylate (VI). The HCl salt of 1-amino-2-hydroxyphenanthrene (VII) in 220 cc. MeOCH₂CH₂OH, 20 cc. 32% HCl and 40 cc. H₂O, treated at 50° with 8 cc. 40% NaNO₂ gave, on direct crystn. a red modification of 1,2-phenanthraquinone-1-diazide (VIIa), C₁₄H₈ON₂ m. 151° (decompn.). Diazotization of VII carried out with AmONO at 25° (or below), with subsequent cooling at about 0°, gave a yellow-green modification (VIIb), small rods, m. 150-1° (decompn.). VIIb could be recrystd. by rapid soln. in warm MeOCH₂CH₂OH contg. a few drops HCl, filtering through C and

treating the filtrate at 60° with 18% HCl to incipient cloudiness. VIII (presumably either form) in dioxane contg. 50% AcOH at 10-18°, **stirred** and irradiated with a Hg vapor lamp gave benz-6,7-indene-3-carboxylic acid, pale ochre, m. 249-50° (decompn.) (from AcOH); Me ester, colorless, m. 139°. Benz-6,7-indene m. 42° (from Et₂O). A mixt. of α -C₁₀H₇CH₂CO₂H (15 g.), 15 g. 2,5-O₂N(MeO)C₆H₃CHO, 45 cc. redistd. Ac₂O, and dry Et₃N under N, heated 12 hrs. at 100° gave 4-hydroxychrysene (IX) (not purified) (cf. Cook and Schoental, C.A. 39, 4603.5). IX (0.6 g.) in 200 cc. EtOH and 20 cc. 10% NaOH at 2° with 1.5 cc. PhN₂Cl (from 1 cc. PhNH₂) gave the 3-phenylazo deriv. of IX, reddish brown **hexagonal** plates, m. 248-9° (from AcOH or dioxane) which on hydrogenation with Raney Ni, soln. in hot HCONMe₂ filtration through C, and treatment with EtOH gave the 3-NH₂ deriv. of IX, colorless **hexagons**, not m. below 400°, 0.4 g. of which in 7.5 cc. HCONMe₂ and 1.25 cc. HCl at 0-5° was treated with 2N NaNO₂ giving 0.37 g. 1,2-chrysenequinone-1-diazide (X) golden yellow, darkening at 150° and charring without m., coupling very slowly with phloroglucinol in NH₄OH giving a red compd. In AcOH, in direct sunlight, X gave naphth[2,1-e]indene-1-carboxylic acid, prismatic rectangles (from AcOH or EtOH) decompg. between 230 and 270° depending on the rate of heating; this on decarboxylation in HCONMe₂ gave cyclopentadienophenanthrene, C₁₇H₁₂, colorless, m. 164-5° giving a blue color with concd. H₂SO₄. 4-Nitroso-5-hydroxy-2-phenyl-2H-benzotriazole (11 g.) (cf. Fries and Roth, C.A. 6, 2413) in EtOH hydrogenated with Raney Ni at 70° and 60 atm. and treated with HCl, gave 5.7 g. HCl salt of the 4-NH₂ analog, C₁₂H₁₀ON₄Cl (sic), cream-colored, m. 257-60°, which in HCONMe₂ with aq. NaNO₂ at 0° gave XI, golden yellow, m. 200-1° (decompn.) (from dioxane), forming an azo dye with phloroglucinol which gave typical metallic lakes; XI, irradiated with a Hg vapor lamp, gave (XII), rectangles, m. 225° (decompn.) (Me ester, m. 119-20°); decarboxylation of which, either by heating directly or in HCONMe₂ gave the corresponding indene, C₁₁H₉N₃, needles, m. 71° (from MeOH). From 5-amino-1-methyl-1H-benzotriazole [Pinnow and Koch, Ber. 30, 2852(1897)] in hot aq. NaOH, with NaNO₂, followed at 0° by the dropwise addn. of 2N H₂SO₄, and subsequently by addn. of an excess concd. H₂SO₄ and heating 5 hrs. at 115-20° (until the mixt. no longer coupled with R acid) there was formed 13.1 g. 5-hydroxy-1-methyl-1H-benzotriazole, C₇H₇ON₃, m. 192-3°. which with HCl and NaNO₂ gave the 4-nitroso deriv., C₇H₆O₂N₄, platelets, decomp. about 227° (from AcOH); this when hydrogenated gave the 4-amino deriv. (XIII) isolated as the HCl salt (XIIIa), C₇H₈ON₄.HCl, colorless prisms (from EtOH contg. HCl) turning yellow on drying, carbonizing gradually at about 210°, and losing HCl when heated 24 hrs. at 125° in a

drying pistol over KOH and P2O5 giving XIII, C7H8ON4, m. 234-6° (decompn.). Treated at 0° with HCl and NaNO2, XIIIa gave (XIV), yellow needles, m. 170-1° (decompn.) (from H2O or EtOH). Irradiated in 300 cc. AcOH and 15 cc. H2O, 1 g. XIV gave 0.55 g. of compd. XV, colorless plates, m. 220-1°, not decarboxylated at 290°, and which failed to react with CH2N2, but which gave a deep red color with "Fast Blue salt BB" (XVI). Deacetylation of XV with 16% HCl gave the HCl salt of the corresponding acid, prisms, hydrolyzing readily to the free acid, C7H7O2N3 (XVII), colorless needles, m. 283-4° (decompn.), giving a play of colors in aq. NaHCO3 (turning from yellow to blue gray to blue-violet), a deep blue color with FeCl3, and a red color when coupled with XVI. XVII was also formed by irradiating XIV in H2O, in the absence of AcOH. XVII was shown to have properties totally different from those of 1-methyl-6,7-dihydroxy-1H-benzotriazole (XVIII). 2,3,4-Br(MeO)2C6H2NO2 and MeNH2 gave the 6-MeNH analog; this was catalytically reduced to 2,3,4-MeNH(MeO)2C6H2NH2 and diazotized, and treated with HBr to give XVIII.HBr, m. 210°. By coupling 1-phenyl-5-hydroxybenzimidazole (XIX) in NaOH and pyridine with p-HO3SC6H4N2Cl followed by acidification, the corresponding (unanalyzed) ochre-colored azo dye was formed, which, in NaOH with Na2S2O4, followed by acidification with AcOH, gave the 4-NH2 deriv. of XIX, colorless prisms, m. 211-12° (decompn.), yielding, on diazotization (XX), yellow, m. 162-3° (from 90% EtOH). Irradiated 2 hrs. in AcOH and H2O, XX gave C15H12O3N2 (XXa), m. 202-6°, contg. an Ac group, and apparently analogous to XV, and, like the latter, could not be decarboxylated by heating in N. 2,4-H2N(O2N)C6H3NHPh (79.6 g.) triturated with 38 g. BzH, heated 15 min. with PhNO2 cooled, and treated with 50 cc. EtOH and HCl gas, gave 58 g. 5-nitro-1,2-diphenylbenzimidazole m. 180-1° (from AcOH) readily reduced to the 5-NH2 analog, m. 191-2°, which, when diazotized in aq. H2SO4 at 0°, followed by heating (until there was no further coupling with R acid), dild. with H2O, and neutralized with NaOH gave the 5-hydroxy analog, C19H14ON2 (XXI), m. 249-50° (decompn.). With p-HO3SC6H4N2Cl, XXI gave the azo dye, C25H18O4N4S (XXII), ochre-colored, charring when heated. XXII in aq. NaOH with Na2S2O4 gave the 4-amino deriv., C19H15ON3 (XXIII), of XXI, m. 206-9°, isolated as the yellow Na salt (XXIIIa), the HCl salt, or as the AcOH salt [C21H19O3N3, pale yellow prisms, m. 211-12°, losing AcOH when kept in vacuo over KOH (giving XXIII)]. XXIIIa (prepd. from 13.5 g. XXII) in 50 cc. 16% HCl, filtered through C, cooled to 0° and treated dropwise with NaNO2 gave the 2-Ph deriv. of XX, orange needles, m. 157-8° (decompn.), which when irradiated in aq. AcOH gave the 2-Ph deriv. (XXIV) of XXa, colorless rhombs, m. 222-3°. 1,2-Naphthoquinone-2-diazide-5-sulfonyl chloride (XXV) (Ger. 865,410) and PhNH2 in C6H6 gave the corresponding

5-sulfanilide (XXVI), $C_{16}H_{11}O_3N_3S$, yellow needles, m. $168-9^{\circ}$ (from C_6H_6 or EtOH), which when irradiated in dioxane contg. HCl gave 4-phenylsulfamoyl-1-indenecarboxylic acid, colorless, m. $183-4^{\circ}$ (decompn.) (from Me_2CO-H_2O), Me ester, m. $188-9^{\circ}$. Prepd. similarly to XXVI was 4-sulfamoyl-1,2-naphthoquinone-2-diazide golden yellow, m. 162° , giving, on irradiation, 3-phenylsulfamoyl-1-indenecarboxylic acid, pale yellow, m. $151-3^{\circ}$ (from AcOEt by the addn. of petr. ether). To 1.6 g. XXVI in 20 cc. dioxane, 3.1 cc. 2N NaOH, and 8 cc. H_2O (at or below 20°) was added 1.6 g. XXV in 10 cc. dioxane, giving N,N-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthylsulfonyl)aniline (XXVII), alkali-insol., m. $145.5-6.0^{\circ}$ (decompn.) (from AcOH). Irradiated at 0° in sunlight, XXVII gave the expected deriv., $C_{26}H_{19}O_8NS_2$, m. $249-50^{\circ}$ (decompn. from AcOH). From Na 6-hydroxy-1,2,3,4-tetrahydro-7-naphthalenesulfonate and p-MeC₆H₄SO₂Cl was formed the 6-tosylate [isolated as the Na salt, m. $128-9^{\circ}$ (decompn.)], converted by PCl₅ into the sulfonyl chloride, $C_{17}H_{17}O_5S_2Cl$, **hexagons**, m. $133-4^{\circ}$, from which was prepd. the 7-sulfanilide, prisms, m. $157-8^{\circ}$; this on sapon. with NaOH in alc. gave 6-hydroxy-1,2,3,4-tetrahydro-7-naphthalenesulfanilide (XXVIII), thin rhombs, m. $183-5^{\circ}$ [Na salt (XXVIIIa), nacreous **hexagons**]. To 38 g. XXVIIIa in 400 cc. 2.5% NaOH, 400 cc. dioxane and 5 cc. pyridine at 0° was added very gradually PhN₂Cl (from 17 g. PhNH₂.HCl), acidified with 30% HCl, and crystd. from dioxane contg. 5% AcOH giving 19 g. 8-PhN₂ deriv. of XXVIII, m. $237-8^{\circ}$ (decompn.), which when reduced with Hoechst Ni catalyst in alc. at 60 atm. and 80° , dissolved in 8% NaOH, washed with Et₂O, filtered through C, and acidified with AcOH gave 9 g. of the 8-NH₂ deriv. of XXVIII, m. 160° (never completely purified because of its ready oxidation), which, by the usual method was converted into the diazide (XXIX) orange-yellow, m. $160-5^{\circ}$ (decompn.), giving, when irradiated 1.5 hrs. in sunlight, XXX, $C_{16}H_{15}NO_3S$, tan amorphous powder. To 12 g. 1,2,3-H₂N(HO)C₁₀H₅CONHPh in 540 cc. EtOH was added 4.2 g. Cu(OAc)₂ in 108 cc. glacial AcOH and 42 cc. 2N NaNO₂; the mixt. warmed to $50-60^{\circ}$ gave the expected oxo-diazo compd., yellow, m. $167-8^{\circ}$ (from AcOH) giving after an 11 hrs. irradiation the indene deriv., $C_{17}H_{13}O_3N$, m. 141° (decompn.) (best purified by soln. in aq. NaHCO₃ and pptn. with HCl); 2-indenecarboxanilide, $C_{16}H_{13}ON$, irregular **hexagons**, m. $180-1^{\circ}$.

CC 10 (Organic Chemistry)

L57 ANSWER 19 OF 20 HCA COPYRIGHT 2004 ACS on STN

42:36467 Original Reference No. 42:7724e-i,7725a The N-substituted derivatives of p-toluenesulfonamide. Cerkovnikov, E.; Tomasic, P. (Institute Hygiene, Zagreb). Arhiv Kem., 19, 38-41; in English, 41-42 (Unavailable) 1947.

GI For diagram(s), see printed CA Issue.

AB The starting material in each case was p-MeC₆H₄SO₂Cl (I) which was treated with the corresponding amine in acetone at comparatively low temps. The product was always dried under a high vacuum over P₂O₅ at 80° about 2 h. for anal. To 19 g. I and 12.2 g. guanidine nitrate in 60 cc. acetone at 0° was added 40 g. 20% NaOH soln. at such a rate that the temp. did not rise above 15°, the mixt. **stirred** 2 h. at room temp., and the product pptd., filtered with suction, and recrystd. from EtOH, giving 8.8 g. (38.1%) N-guanyl-p-toluenesulfonamide, C₈H₁₁N₂O₂S.H₂O, m. 207-8°, crystd. like sulfaguanidine with 1 mol. water. The same method as above, using 60 cc. solvent, 19 g. I, 9.4 g. 2-aminopyridine, and 20 g. NaOH soln., gave 9.0 g. (36.3%) N-2-pyridyl-p-toluenesulfonamide, C₁₂H₁₂O₂N₂S, needles from MeOH, m. 213-14°. From 19 g. I and 9.5 g. 2-amino-4-methylpyrimidine in 60 cc. acetone in the presence of 20 g. 20% NaOH, 9.0 g. (34.2%) N-(4-methyl-2-pyrimidyl)-p-toluenesulfonamide, C₁₂H₁₃O₂N₃S, **hexagonal** prisms from H₂O, m. 226.5-8°, was obtained. The condensation product, C₁₇H₁₆N₂O₄S₃ (II), of I and 2-aminothiazole (1.2 g. from 5.7 g. I and 3.0 g. 2-aminothiazole in 18 cc. acetone and 6 g. 20% NaOH) m. 150-1° (from EtOH). The 2-aminothiazole used reacted in its tautomeric form and all attempts to prep. N-2-thiazolyl-p-toluenesulfonamide failed. N - 8 - Quinolyl - p - toluenesulfonamide, C₁₆H₁₄O₂N₂S (20.2 g. crude product (67.8%) from 19.0 g. I and 14.4 g. 8-aminoquinoline in 60 cc. acetone with 20 g. 20% NaOH), tetrahedrons from acetone, m. 153°. N-(6-Methoxy-8-quinolyl)-p-toluenesulfonamide, C₁₇H₁₆O₃N₂S (4 g. crude product (61%) from 3.8 g. I and 3.5 g. 8-amino-6-methoxyquinoline in 12 cc. acetone with 4 g. 20% NaOH) in. 131-2° (from acetone). All above compds. were tested in vitro against the different strains of the dysentery bacillus (Schiga, Schmitz, Flexner II and III, Boyd I and V). They were also tested against streptococcus and pneumococcus (types not stated). The method of culturing in solid media was used in each case. None of these compds. in a 2% soln. was found bacteriostatic against any one of the listed pathogenic organisms. 8 refs..

CC 10 (Organic Chemistry)

L57 ANSWER 20 OF 20 HCA COPYRIGHT 2004 ACS on STN

14:15544 Original Reference No. 14:2893h-i,2894a-i,2895a-i,2896a Contribution to the chemistry of phosphomolybdic acids, phosphotungstic acids and allied substances. Wu, Hsein Journal of Biological Chemistry, 43, 189-220 (Unavailable) 1920. CODEN: JBCHA3. ISSN: 0021-9258.

AB Allowing M to represent Mo or W, the complex H₃PO₄ compds. of these elements fall into 2 groups: 1. Acids containing 1 mol. P₂O₅ to 18 or to 24 mols. MO₃, known in this abstract as 18-or 24-acids, resp., which are colored except for the 24-W compd., are sensitive

to reduction and are pptd. by pyridine in dil. soln. In alk. soln. they are converted into substances of group 2. These are salts with a number of different $P_2O_5:MO_3$ ratios, all are colorless, do not ppt. pyridine in dil. soln., are not sensitive to reduction and are converted by mineral acids of group 1. The formation of the complex acids depends upon the concn. of the reacting substances, the temp. and the acidity. The concns. affect the result according to the laws of mass action; the 24-acids may be formed at room temp. but 18-acids require boiling. The most important factor is the acidity. H_3PO_4 and Na_2MoO_4 , mixed in any proportion, will not form a complex acid. The addition of HCl equiv. to the Na_2MoO_4 is followed by the formation of a mixt. of the 18- and 24-acids. The yield of the latter increases with the acidity. In a mixt. of 1 mol. Na_2WO_4 and 4 mols. H_3PO_4 , all the W is converted into the 18-acid. If HCl be added, the 24-acid is formed almost exclusively. The Mo acids are readily interconvertible; the W acids are more stable. Phospho-24-molybdic acid. Dissolve 100 g. $Na_2MoO_4 \cdot 2H_2O$ in 200 cc. H_2O , add 10 cc. 85% H_3PO_4 , 100 cc. concd. HCl and 150 cc. Et_2O and shake in a 1. sepg. funnel. Cool. After 10-5 min. transfer the lowest of the 3 layers to another funnel. Add 100 CC. H_2O , shake; add 50 cc. concd. HCl and some more Et_2O and shake again. Cool and again remove lowest layer and repeat the washing. Transfer to a beaker, add 25 cc. H_2O and a few drops concd. HNO_3 and evap. on the H_2O -bath until crystals form on the surface. Allow to cool slowly. Yellow octahedra, $3H_2O \cdot P_2O_5 \cdot 24MoO_3 + 59H_2O$. Phospho-18-molybdic acid. Dissolve 100 g. $Na_2MoO_4 \cdot 2H_2O$ in 450 cc. H_2O , add 15 cc. 85% H_3PO_4 and 80 cc. concd. HCl and boil for 8 hrs. with reflux. Cool. **Stir** in 100 g. powdered NH_4Cl . Filter as dry as possible on a Buchner filter. Dissolve in an equal wt. of H_2O and filter off the NH_4 salt of the 24-acid on hardened paper. Add 20% NH_4Cl without stirring, let stand 4-8 hrs., filter dry as possible on a Buchner filter, dissolve in a little H_2O and evap. in vacuo at not over 40° until crystals begin to form. Cool slowly to $5-6^\circ$. Filter dry as possible. Disconnect the suction, cover the crystals with dry Et_2O , **Stir**, let stand a few min., and suck dry. Dry quickly. Orange crystals, $3(NH_4)_2O \cdot P_2O_5 \cdot 18MoO_3 \cdot 11H_2O$. The free acid is liberated with concd. HCl , is extd. with Et_2O washed and evapd. as in case of the 24-acid, but at low temp. (20°). Orange prisms, $3H_2O \cdot P_2O_5 \cdot 18MoO_3 \cdot 11H_2O$. Phospho-24-tungstic acid. Dissolve 100 g. $Na_2WO_4 \cdot 2H_2O$ in 100 cc. warm H_2O , add 10 cc. 85% H_3PO_4 and 80 cc. concd. HCl . Allow to cool and after at least 4 hrs. filter as dry as possible, redissolve in 120 cc. H_2O add 70 cc. Et_2O and 40 cc. concd. HCl and extract, wash and evap. as in case of the 24-Mo acid. Colorless octahedra, $3H_2O \cdot P_2O_5 \cdot 24WO_3 \cdot 59H_2O$. This is the chief ingredient of the comm. phosphotungstic acid, which is not pure, the Merck and Kahl-baum. preps. containing 10% of the 18-acid. Phospho-18-tungstic acid exists in 2 forms, A and B.

Dissolve 200 g. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in 1000 cc. H_2O . Add 280 g. 85% H_3PO_4 and boil for 8 hrs. under a reflux, allowing the soln. to evap. to 1000 cc. toward the end of this period. Add a few drops $\text{Br-H}_2\text{O}$, cool and add 200 g. powdered NH_4Cl **Stir** and filter on a Buchner filter. Dissolve in H_2O and reppt. with NH_4Cl . Repeat. Dissolve in 600 cc. H_2O at 50° and keep at 37° . Crystals of NH_4 A-phospho-18-tung-state sep. in a few days. When no more form, decant the liquid, wash the crystals with ice-cold H_2O and recryst. 5 times from H_2O . Yield 30 g. of tough, lemon-yellow crystals, $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 18\text{WO}_3 \cdot 16\text{H}_2\text{O}$, **hexagonal** prisms terminated by 1 or 2 rhom-bohedra, which do not readily lose H_2O of crystn., soly. 51 g. in 100 g. H_2O ; the B form, $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 18\text{WO}_3 \cdot 18\text{H}_2\text{O}$, crystallizes on longer standing; it consists of thin, brittle, pale yellow, rhomboidal plates with truncated edges, which easily lose H_2O . Soly. 122 g. in 100 g. H_2O . The A form yields 30% more blue color when treated with uric acid and Na_2CO_3 : than does B. The color developed by the former has a tint of green, that by B, violet. The acids are set free by HCl , extd. with Et_2O and evapd. on the H_2O bath. A-Phospho-18-tungstic acid, $\text{P}_2\text{O}_5 \cdot 18\text{WO}_3 \cdot 38\text{H}_2\text{O}$. B-Phospho-18-tungstic acid, $\text{P}_2\text{O}_5 \cdot 18\text{WO}_3 \cdot 40\text{H}_2\text{O}$. The methods for analysis of the complex phosphotungstic and -molybdic acids were: **P205**; Dissolve 2.5-3 g. material in 25 cc. warm H_2O , add 25-30 cc. 10% NaOH , heat to boiling until the ppt. has redissolved and then at slightly lower temp. for 20 min. longer. Cool and add 5-6 g. NH_4Cl , 10-15 cc. magnesia mixt. (55 g. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 140 g. NH_4Cl and 350 cc. concd. NH_4OH per liter) and 0.25 vol. concd. NH_4OH . After 4 hrs. filter and wash with 1:4 NH_4OH . Ignite the ppt., digest the ash with 15 cc. 2N HCl for 1 hr. at $80-90^\circ$, filter on a small paper and wash with ten-cc. portions of 0.5 N HCl . Add 5 cc. magnesia mixt. and, very slowly, 25 cc. concd. NH_4OH . Filter after 4 hrs., wash with 1:4 NH_4OH , ignite and weigh. Correct for blank. If no W, but only Mo, is present, the heating with NaOH and the double pptn. may be omitted, for the complex acid is decompd. by NH_4OH at ordinary temp. WO_3 : On ignition, P is always lost, so that the correct WO_3 content is detd. by weighing the ignited residue, detg. the **P205** content therein as above and subtracting. NH_3 is detd. by distn. and H_2O by difference. A number of the mixed complex acids, containing both Mo and W, were also prepd. by essentially the same methods. In general, their properties resemble those of the corresponding acid containing only the predominant element. The sensitivity to reduction with Na_2SO_3 , is roughly parallel to the Mo content. The color changes from bluish green to violet as the proportion of W is increased. The 24-acids were not investigated in detail. The "phenol reagent" of Folin and Denis (cf. C. A. 6, 2245; 13, 2541, 2545) is one of the mixed 18-acids and these were studied more carefully. In the absence of a strong acid, the acid formed contains much W and is not sensitive to reduction, no matter how

much MoO_3 is used. The greater the amt. of MoO_3 to be incorporated, the greater is the concn. of HCl required. If too much HCl is used, some 24-acid may be formed. The acid of the "phenol reagent" is prepd. as follows: Dissolve 100 g. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 25 g. $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in 700 cc. H_2O . Add 50 cc. 85% H_3PO_4 and 100 cc. concd. HCl . Boil under a reflux for 8 hrs. (Dil. for use as reagent.) Sat. the cooled soln. with NH_4Cl , filter, redissolve in warm H_2O and filter off the yellow insol. residue. If the NH_4 salt is desired, salt out again and recryst. from warm H_2O . It consists of a mixt. of $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 13\text{WO}_3 \cdot 5\text{MoO}_3 \cdot 10\text{H}_2\text{O}$ and $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 14\text{WO}_3 \cdot 4\text{MoO}_3 \cdot 10\text{H}_2\text{O}$. The free acids are obtained in Et_2O soln. as usual and the soln. is evapd. at low temp. A number of NH_4 salts of the reduced phosphomolybdic acids were also prepd., the extent of the reduction being detd. by titration with KMnO_4 . The method of reduction is indicated. $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 17\text{MoO}_3 \cdot \text{MoO}_2 \cdot \text{H}_2\text{O}$, excess of Fe^{++} in acid soln., 20% NH_4Cl , black crystals. $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 16\text{MoO}_3 \cdot 2\text{MoO}_2 \cdot \text{H}_2\text{O}$, from 10 g. NH_4 salt of 18-acid, 50 cc. H_2O , 5 cc. 40% HI and 5 g. NaHSO_3 , standing 24 hrs., 10 g. NH_4Cl , black crystals. $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 16\text{MoO}_3 \cdot \text{Mo}_2\text{O}_5 \cdot \text{H}_2\text{O}$, from 10 g. NH_4 salt of 18-acid, 50 cc. H_2O , 5 cc. 40% HI , satn. with H_2S , standing 24 hrs., 10 g. NH_4Cl , black crystals, violet reflex. $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 22\text{MoO}_3 \cdot 2\text{MoO}_2 \cdot \text{H}_2\text{O}$, 10 g. of the 24-acid, 50 cc. H_2O , 5 cc. 40% HI and 5 g. NaHSO_3 , 10g. NH_4Cl at once, blue powder. $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 2\text{MoO}_3 \cdot 4\text{MoO}_2 \cdot \text{H}_2\text{O}$, as preceding, but standing 24 hrs. before adding NH_4Cl , black ppt. A number of interesting applications of these complex acids in analytical chemistry are indicated. Detection of Cu : Add a few drops 5% KCN , acidify with HCl , add a few drops "phenol reagent." If more than a trace of Cu is present the mixt. will become blue at once; otherwise it is yellow but becomes blue on addition of Na_2CO_3 ; sensitivity, 1:5,000,000. Detection of P_2O_5 : Add 1-2 CC. 2% $(\text{NH}_4)_2\text{MoO}_4$ soln., 2-3 CC. 10% KI , 1 cc. 10% NaHSO_3 and 1-2 cc. concd. HCl , After 10-20 min. make alk. with Na_2CO_3 ; blue color indicates P_2O_5 . Sensitivity, 1:1,000,000 of P . Deln. of P_2O_5 : To the unknown soln. containing 0.1 to 0.2 mg. P in 5 cc. in a 50-cc. flask, add 5 cc. each of 10% NaHSO_3 , 10% KI , 2% $(\text{NH}_4)_2\text{MoO}_4$ and 1:1 HCl . Similarly treat 5 cc. of standard soln. containing 0.15 mg. P . Cover the, flasks and allow to stand 2 hrs. Add to each 10 cc. 20% Na_2CO_3 , shake to hasten the escape of CO_2 , dil. to 50 cc. and compare in a colorimeter. The color developed is not max., but is proportional to the amt. of P within the range 0.1-0.22 mg. Application to oxidation-reduction reactions in presence of F^{++} is also indicated.

CC 6 (Inorganic Chemistry)